ANNUAL REPORT

1968-69

National Chemical Laboratory, Poona

NATIONAL CHEMICAL LABORATORY
POONA
1968-1969

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

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INTRODUCTION

The report covers the period April 1968-March 1969 and presents the progress of R & D projects classified under the four heads: sponsored projects, pilot plant projects, product-oriented research and basic/applied basic research schemes.

During 1968-69, work on 15 sponsored projects has been completed and 6 new schemes undertaken. Currently (August 1969), work on 19 sponsored research schemes is in progress. Of these, 13 are sponsored by industry, 4 by State and Central Government Agencies, and 2 are being supported from the PL-480 funds. The total receipts from sponsored projects for the year 1968-69 were Rs. 6·22 lakhs.

Five pilot plant projects were operated during the year under review. Based on NCL pilot plant studies, a proposal for a turn-key plant designed to produce 600 TPA of aniline is being offered to HOC, Rasayani, through a firm of project engineers. A multi-purpose pilot plant project on various organic chemicals and intermediates is in progress.

Out of the 89 schemes on product-oriented research, 7 are in the field of solid state materials, 10 on synthetic inorganic and organo-metallic products, 38 are on natural and synthetic organic chemicals, 28 relate to rubber and other polymeric materials and 6 concern the development of instruments. It will be seen from the various research schemes described in the fourth section that the Laboratory is also actively engaged in basic research in many disciplines of chemistry and chemical technology. As a result, 114 research papers have been published in Indian and foreign journals and 27 scientists (17, Research Fellows and 10 staff members) received Ph.D. degrees during the year

Work done on account of services rendered to outside parties, processes released during the year, sponsored projects completed, publications, patents etc., is described in the Appendices at the end of the report.

Tables at the end give details of 1968-69 production of various products manufactured on the basis of NCL know-how, processes so far released and awaiting production, and processes ready for release. Whereas the value of such production of 29 items for the year 1967-68 was Rs. 40 lakhs, during the year under review this increased to Rs. 70 lakhs (47 items). Of the latter, Rs. 24·5 lakhs may be regarded as the laboratory's contribution to saving in foreign exchange. There has also been foreign exchange earnings of Rs. 4·73 lakhs through export of β-ionone.

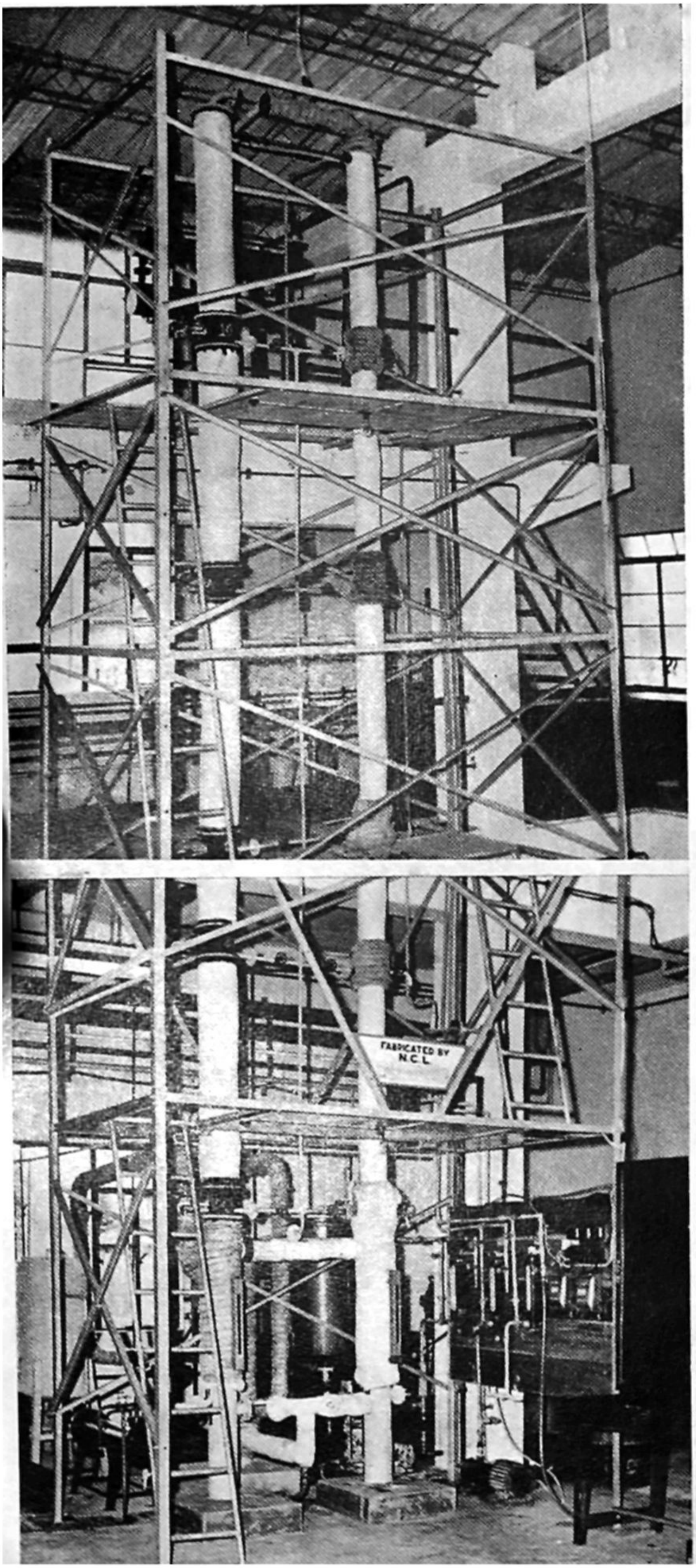
A separate table enlists the 29 processes approved so far by the NCL Process Release Committee (functioning since September 1967); five of these processes have already been released to industry and negotiations for the others are in progress.

Data on inputs and receipts by way of rendering analytical service, technical aid, share of premia and royalities, technical consultancy and fees for sponsored projects are also presented in the Appendices.

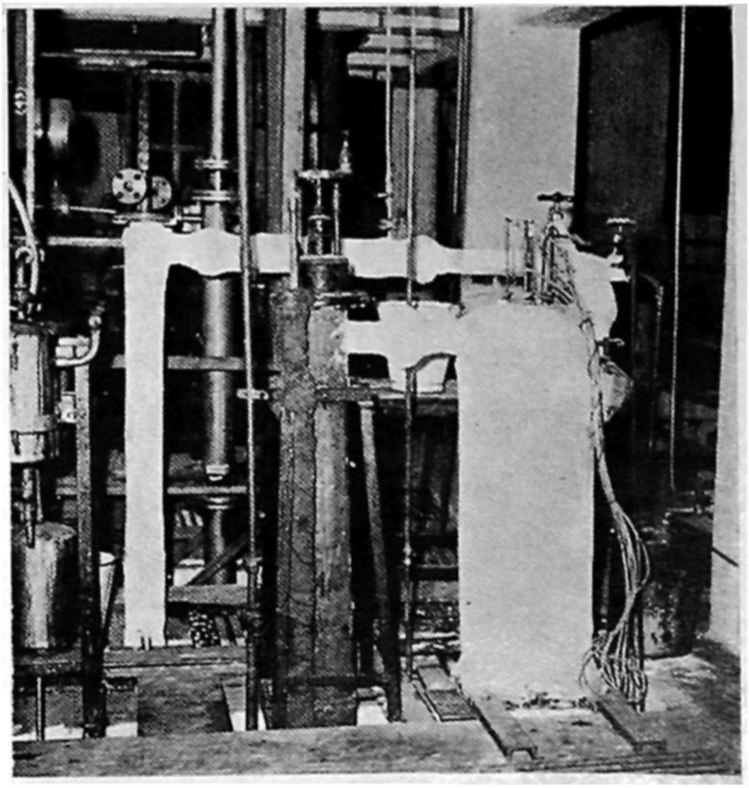
CSIR SILVER JUBILEE CELEBRATIONS AT NCL
(AUGUST 1968)

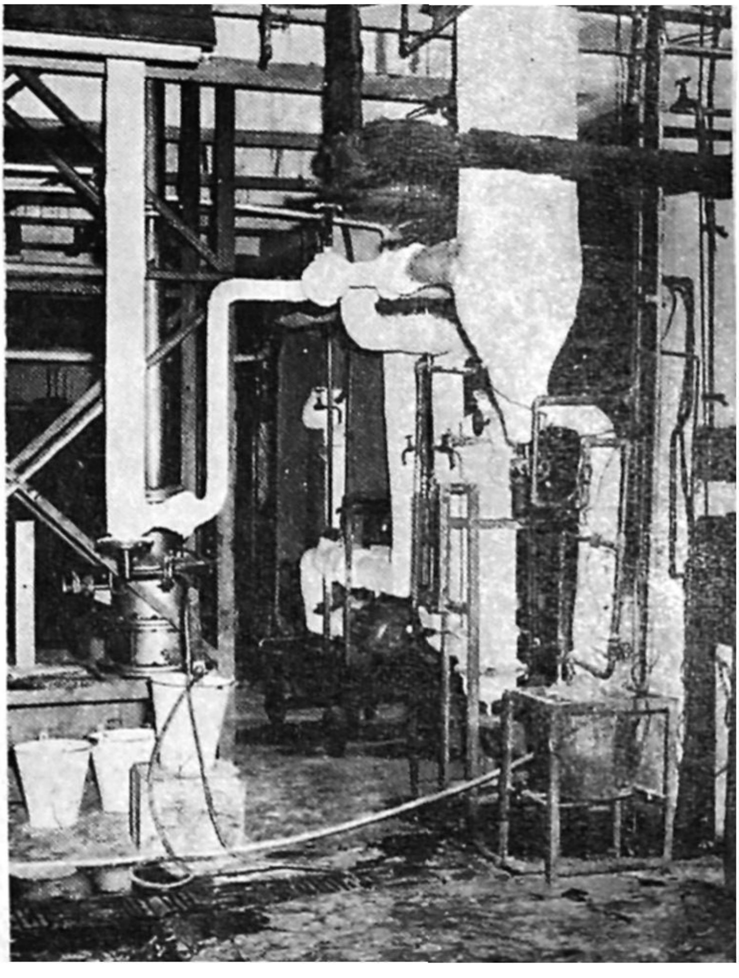
NIGHT ILLUMINATIONS OF NCL MAIN BUILDING

NCL SCIENTISTS
(DR. N. L. DUTTA, DR. J. L. BOSE)
RECEIVED 'SILVER JUBILEE
SERVICE AWARDS'

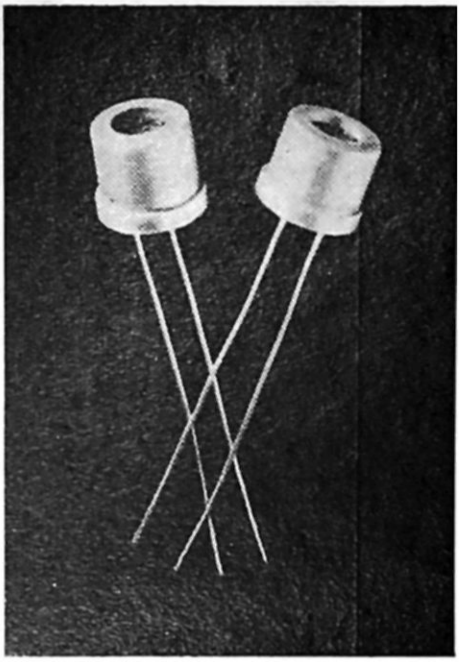


CHLOROBENZENE
PILOT PLANT AT NCL

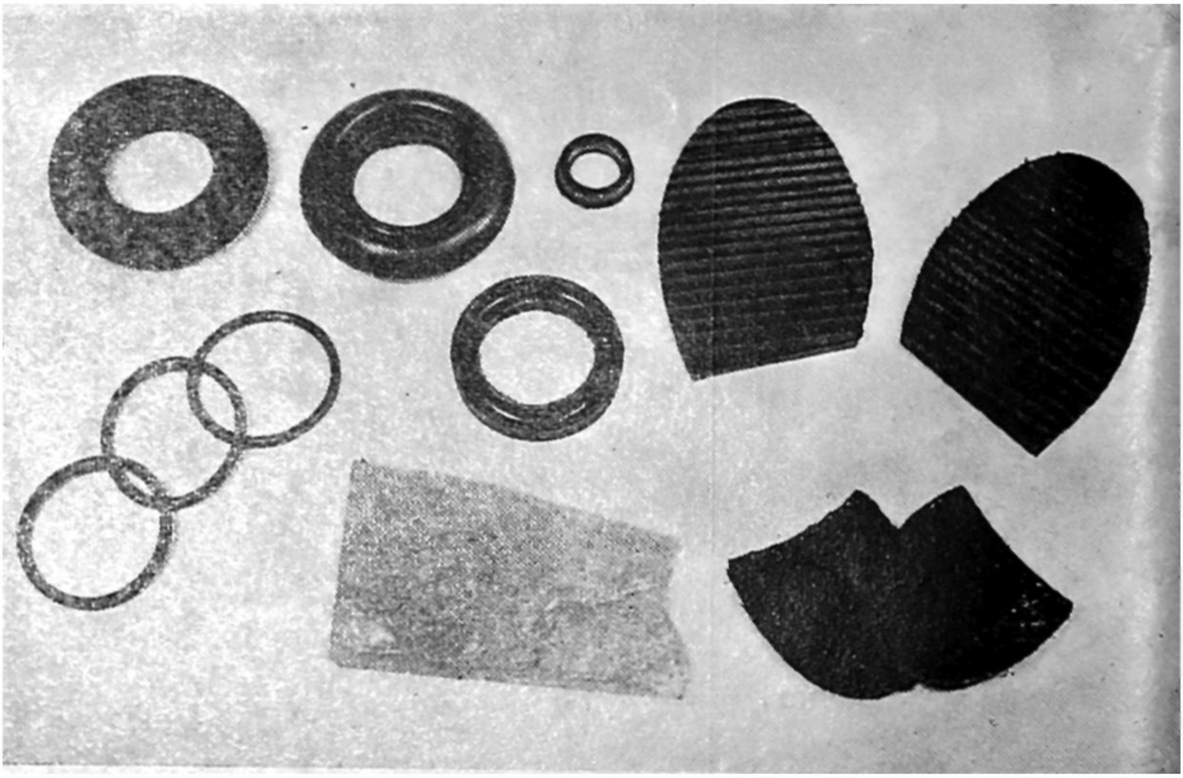




ANILINE PILOT PLANT AT NCL



CdS PHOTOCONDUCTIVE CELLS



POLYURETHANE-BASED SYNTHETIC POLYMERS

SPONSORED PROJECTS

PRIVATE PARTIES

INTERMEDIATES AND DYES

1. *Anthraquinonoid intermediates and dyes :* (SP-18/66)

The work consisted mainly of developing chromatographic and spectroscopic methods for ascertaining chemical purity of a wide range of intermediates used in the preparation of important vat, acid and reactive dyes. It has been found that the absorption spectrum can be used for the quantitative evaluation of Bromamine acid, an important intermediate for the preparation of acid, disperse and reactive dyes. The analytical methods developed can be used for following the course of reactions and also for quality control. The scheme is concluded.

TERPENOIDS

2. *Utilization of longifolene and Δ^3-carene :* (SP-15/66)

The Indian turpentine oil (*ex-Pinus longifolia*) contains nearly 20% of pinenes and large quantities of longifolene and Δ^3-carene. In order to utilize the Indian turpentine oil as a raw material for industrial products, developmental work for the utilization of longifolene and Δ^3-carene was undertaken.

A number of products from longifolene and Δ^3-carene were prepared and sent to the sponsor for evaluation. The preparation of a derivative based on longifolene was optimized and the details furnished to the sponsor. Some of the derivatives obtained from Δ^3-carene, which were supplied to the sponsor, showed perfumery acceptability. Hence these were prepared on a relatively large scale and sent to the sponsor for market evaluation. The process for the preparation of these compounds was also standardized. The scheme is concluded.

3. *Isolation of borneol :* (SP-41/68)

Isoborneol is obtained as an intermediate in the commercial preparation of camphor from pinene. Borneol and isoborneol are at present the only bicyclic terpene compounds used extensively in the perfumery industry. The acetate of isoborneol is a popular perfumery material for soaps, cleaning fluids, etc. However, borneol and its ester have a finer and more natural fragrance than isoborneol and its derivatives and are preferred by perfumers.

A simple procedure for the preparation of isobornyl acetate has been developed and the know-how supplied to the sponsor. The isomerization of isoborneol to borneol has been studied in detail for ultimately developing a process for the preparation of borneol.

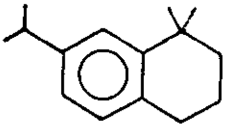
4. *Utilization of isolongifolene :* (SP-44/68)

Isolongifolene, a sesquiterpene artefact, is the major bye-product obtained in certain reactions of longifolene. Attempts were, therefore, made to obtain useful industrial products from isolongifolene.

One of the reactions of isolongifolene furnished a product having a pleasant smell. A sample of this product has been supplied to the sponsor for evaluating it as a perfumery chemical.

Work on standardizing the process for the preparation of the new product and elucidating its structure is in progress.

During this work a further rearrangement of isolongifolene has been observed. The major hydrocarbon obtained is a tetralin derivative.



I

DRUGS AND PHARMACEUTICALS

5. *Carbimazole :* (SP-11/65)

This drug is used in the treatment of hyperthyroidism and *angina pectoris*. It is considerably less toxic than most of the drugs used in the field. Conditions for the technical preparation were successfully established on large batches. However, at the instance of the sponsor, the procedure is being modified wherein the use of a particular chemical is avoided. Trials to this effect are in progress.

6. *Megimide :* (SP-36/67)

This drug is used as an antidote in the treatment of barbiturate poisoning and to terminate barbiturate anaesthesia.

Preparations were carried out on laboratory scale and a product meeting B. P. specifications was obtained. The method of preparation is being standardized on bench scale according to the sponsor's requirement.

7. *Sorbide nitrate :* (SP-13/65)

Isosorbide dinitrate is a coronary vasodilator used in the treatment of *angina pectoris.*

Conditions for the preparation of this drug were standarized on a large batch size. The product is regularly manufactured in the sponsor's factory after successful conclusion of the scheme.

8. *Sulphacetamide and its sodium salt :* (SP-12/65)

Sulphacetamide sodium is mainly used in the form of a solution or an ointment in the treatment of eye infections.

After standardizing the process on a scale of 3 kg./batch, work on this product is temporarily suspended because of the higher priority placed by the sponsor on some other drugs.

9. *8-Hydroxyquinoline :* (SP-43/68)

This is an important intermediate for the manufacture of anti-dysentery drugs. Several experiments were carried out on laboratory scale and good yields have been obtained. Scale up work on pilot plant is in progress.

10. *Radio-opaque dyes :* (SP-14/66)

This work was undertaken to develop know-how for the synthesis of some of the important radio-opaque dyes like diatrizoic acid and iodipamide which are the main ingredients of well known preparations like urografin, biligrafin and endografin. The X-ray contrast caused by these dyes is essential for radiological diagnosis. The entire requirement of the country for these dyes is met by imports at present.

Work was also undertaken to develop a method for the production of methylglucamine required for solubilization of these dyes for intravenous administration.

The work on the synthesis of the required radio-opaque dyes and methylglucamine has been successfully concluded in large laboratory scale experiments and final reports have been submitted to the sponsor. The firm is likely to produce them in the near future in sufficient quantities to meet the entire demand of the country.

PERFUMERY CHEMICALS

11. *β-Phenethyl alcohol :* (SP-31/67)

Laboratory scale preparation of β-phenethyl alcohol has been standardized and the preparation was demonstrated to the party.

Pilot plant runs on a 120-litre reactor have been started. The basic design of the reactor, set up with other ancillary equipment, is found to work satisfactorily. The effects of various process conditions are being studied to get optimum product yield. The product obtained from the pilot plant experiment was found to satisfy all physical tests. Necessary process data will be collected to prepare chemical engineering designs for a commercial plant of about 50 tonnes/year in the first instance.

12. *Preparation of perfumery grade geraniol, citronellal and citronellol from Indian lemongrass oil :* (SP-32/68)

Geraniol, citronellal and citronellol are widely used in the perfumery industry. The above chemicals are being prepared from imported citronella oil from Java.

Optimum conditions for the preparation of perfumery grade geraniol, citronellal and citronellol on a laboratory scale from Indian lemongrass oil have been established. The scheme is concluded.

MISCELLANEOUS

13. *Analysis of organic compositions of industrial importance:* (SP-33/68)

A number of special organic compositions available under different trade names are used in various industries. Many of these are imported. Identification of these compositions is undertaken with a view to explore the feasibility of manufacture of similar compositions from indigenous raw materials.

During the period under report, a sample of a textile auxiliary material has been analysed and the composition reported to the party.

Analytical examination of three surface active agents is in progress.

14. *Screening of NCL compounds by Bristol Laboratories, Syracuse, (N. Y.), for pharmacological activity :* (SP-35/67)

Under this scheme, organic compounds isolated or synthesized in the NCL are sent for biological testing and evaluation.

During the period under report, thirty compounds have been sent from NCL to Bristol Laboratories for evaluation.

15. *Steroids and wax from sugarcane press-mud :* (SP-37/67)

The press-mud, obtained plentifully from the Indian Sugar Mills following the sulphitation process, contains appreciable quantities of stigma- and sito-sterols, and a wax. Procedures are already known for the extraction of crude sugarcane wax from the press-mud, but the isolation of sterols after extraction of the wax is extremely difficult. It has been established that the sterol mixture can be more conveniently isolated directly from the press-mud prior to the extraction of sugarcane wax.

Several hundred kilos of press-mud, supplied by the sponsor, were processed by a new procedure, and the sterol mixture and a superior quality of sugarcane wax have been extracted. The extracted products and the process details have been supplied to the sponsor. The project is concluded.

16. *Development of adhesives for decorative laminates :* (SP-42/68)

The decorative laminated sheets have a natural tendency of lifting at the ends. This poses a problem for adhesion of these sheets to furniture.

The work has been undertaken to develop a suitable adhesive formulation satisfying certain specifications laid down by the sponsor.

An adhesive formulation was developed which was found to satisfy laboratory tests for small sheets. The product is being evaluated by the sponsor. The scheme is concluded.

17. *Technical preparation of liquid stabilizer for PVC :* (SP-47/68)

Although PVC is manufactured in the country, stabilizers for PVC are still imported. The total requirement of various PVC stabilizers in the country is of the order of 200 TPA.

A liquid stabilizer based on indigenous materials is being developed.

18. *Technical preparation of pentachlorophenol and other chlorophenolic compounds :* (SP-8/67)

Pentachlorophenol, widely used as a wood preservative and fungicide, is prepared by the chlorination of phenol. Bench scale studies for the preparation of pentachlorophenol have been completed and pilot plant studies undertaken. Several batches have been taken on 15 kg. scale.

o-Chloro-*m*-xylenol and dichloro-*m*-xylenol, used as general antiseptic and germicide, are prepared by the mono- and di-chlorination of *m*-xylenol respectively. These were prepared in the laboratory by the chlorination of commercially available tar acids.

In the analysis of the reaction products from the chlorination of various xylenols, several chloroxylenols of authentic structure were needed for analytical comparison. The programme of preparing samples of pure isomers has been started. Further work on the analysis of pure xylenols and of commercially available tar acids is in progress.

19. *Development of an infra-red spectrophotometer :* (SP-45/68)

Work on the following systems of the IR spectrophotometer has been completed:

(i) Optical nulling system

(ii) Detector and associated electronic system

(iii) The electronics system console

(iv) Evaluation of optical servo system

A new IR detector system which gives several times the sensitivity of previous detectors has been developed. A patent application is being filed for this new system.

An optical servo system which is considerably faster than the systems used in other IR spectrophotometers has been devised.

Work on the monochrometer and assembly of the various units into a complete instrument is in progress.

CENTRAL AND STATE GOVERNMENT INSTITUTES

20. *Composite drug research scheme on Indian medicinal plants :* (SP-23/65)

Under this scheme, the chemistry of pharmacologically active extracts of some of the well-known Indian medicinal plants is being studied. The isolated individual components are sent to another unit for pharmacological testing.

In all three species *Caesalpinia bounducella Flem* (Putikaranja), *Asparagus racemosus Willd* (Shatavari) and *Boerhavia diffusa Linn* (Punarnava), have been under study.

From the defatted seed kernels of Putikaranja, two new diterpenoids were isolated and tentative structures were assigned to them on spectral evidence. From the roots of Shatavari a mixture of saponins was isolated. From the hydrolyzed saponins sarsapogenin was identified. A comparative TLC of various extracts of *Boerhavia diffusa* and *B. punarnava* revealed that the chemical constituents in both are essentially the same. Diuretic action was found for both the acidic and neutral fractions of petroleum ether extracts of the roots.

During the year under report, work on the isolation of active constituents from (a) the roots of *Curculigo orchiodes* (Kali Musli) and (b) the leaves of *Melia azadirachta* (Neem) has been undertaken.

Juice from the leaves of *Bryophyllum calicinum* was extracted and tested for anti-bacterial properties. Contrary to literature claim of high activity, the juice was found to be quite unpromising and so chemical investigation of the same was not pursued.

21. *Fabrication of Electron Diffraction Camera :* (SP-21/65)

The project includes designing and fabrication of the electron diffraction camera and asssociated accessories. Fabrication of one unit each for Gauhati University, Gauhati; Fertilizer Corporation of India, Sindri, and Defence Science Laboratory, New Delhi, has been undertaken.

One of the electron diffraction cameras has been fully tested and is ready for despatch. The other two are under test before despatch.

22. *Constitution of lac :* (SP 24/61) (AB-49/68)

Work has been undertaken to study the chemical constitution of the lac resin which has so far remained unsolved. It is likely that this study may also result in opening new fields of utilization for the indigenous and plentifully available natural resin.

It has been established that the chief building blocks of the lac resin are jalaric and aleuritic acids. The structures for the lac acids derived from jalaric acid have been elucidated. Oxidation, hydrolysis and degradation sequence have afforded useful information on the linking of the component acids of lac molecule.

Taking into consideration the structural similarity of a new aldehydic lac acid with that of jalaric acid, the new acid has been named 'lacci-jalaric acid'. A direct chemical correlation of this acid with $(-)$ α-cedrene has been accomplished for the first time. Out of the terpenic acid moles (six) present in the molecule of pure fraction, the proportion of jalaric to lacci-jalaric series is 5 : 1.

A tentative structure for the lac molecule of pure fraction, which satisfies the data obtained so far, has been put forth.

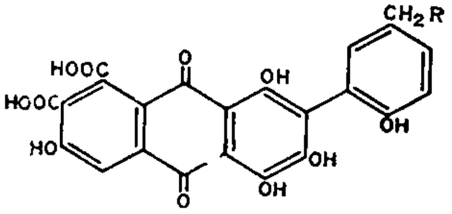
Good progress was made to isolate from lac, pure esters consisting of two moles of component acids. The structures of these esters are being studied following standard procedures. This information will be useful in establishing the final structure of the pure fraction of lac.

23. *Lac dye :* (SP-25/57)

The colouring matter of lac is under investigation. The isolation and determination of the constitution of major constituents of lac dye were reported earlier. The structure of laccaic acid A (the nitrogen-containing compound) was shown to be (I) and the non-nitrogenous laccaic acid B was formulated as (II). These two pigments constitute about 80% of the total dye.

Laccaic acid C has the structure (III), and it is the first naturally occurring anthraquinone carrying an amino acid side chain. In the biosynthetic scheme which has been suggested for some insect pigments derived from anthraquinone (*Tetrahedron Letters* 2223, 1968), laccaic acid C formed by the oxidative coupling of a purpurin derivative with tyrosine can also be included.

Laccaic acid E is probably deacetyl laccaic acid A; it was possible to isolate it entirely free from laccaic acid C, but acetylation of laccaic acid E and hydrolysis of the *o*-acetyl groups gave a product chromatographically identical with laccaic acid A.



I R = CH_2NHAc
II R = CH_2-OH
III R = $\underset{\displaystyle NH_2}{CH}$-COOH

A serious problem concerning any attempts to utilize lac dye is the wide variation in the dye content of different stick lacs. The stick lac received from M/s. Angelo Brothers, Calcutta, was found to yield only 0·1% of dye by the standard procedure, which consists in extraction with water, passage of the aqueous solution through a column of CNSL resin, adsorption of the dye on polyamide powder, elution with butanolic hydrochloric acid, extraction with bicarbonate solution and acidification.

Stick lac from Thailand was found to contain the same laccaic acids as Indian stick lac. In addition, minute quantities of kermesic acid, emodin and an anthraquinone pigment of undetermined structure were isolated.

24. *Titanium tetrachloride from ilmenite :* (SP-22/65)

This work was initiated to study the pilot plant production of $TiCl_4$ from Kerala ilmenite. The product ($TiCl_4$) is to be used to prepare rutile titania which in turn will be employed as a seed material in the sulphate process for the production of high grade TiO_2 pigment.

On the basis of the know-how developed at the NCL, a pilot plant to produce 500 kg. $TiCl_4$ per day has been installed at Trivandrum at the factory site of M/s. Travancore Titanium Products Ltd. The beneficiation and leaching units are working, and the chlorination unit will go on stream shortly. The project has been concluded.

25. *Pulping of Kashmir soft woods :* (SP-30/67)

The scheme was undertaken to determine the suitability of some of the Kashmir soft woods for the manufacture of rayon grade pulp, rayon yarn and for establishing the process conditions for the manufacture of high grade dissolving pulp.

The results have proved that pulps suitable for rayon apparel yarn could be produced from the woods by prehydrolysis sulphate process, while pulps produced by sulphite process, although, found suitable for rayon apparel yarn are of medium grade.

This scheme was renewed in December, 1968, mainly to find out economic ways of producing pulps of higher purity which will be suitable for the manufacture of rayon tyre cord.

PL-480 SCHEMES

26. *Chemical and thermodynamic properties of refractory materials at high temperatures :* (SP-27/64)

The chemistry of refractory oxides, sulphides and nitrides of Al, Ce, La, etc., at high temperatures is of interest in several important fields like ceramics, materials for rocketry, atomic energy, etc. Thermodynamic properties of some of the above materials are being investigated employing transpiration, Langmuir free evaporation and Knudsen cell effusion techniques.

In the last four years, studies in gas-solid reactions at high temperatures were completed and the results published. These studies would help the estimation of thermodynamic properties such as heats of formation, entropy of unstable species viz., $AlCl(g)$, $MnCl(g)$, $AlOCl(g)$ as well as of solid spinels such as $MgAl_2O_4(c)$ and $NiAl_2O_4(c)$.

A high temperature vacuum micro-balance has been fabricated and preliminary runs have been statisfactorily carried out at temperatures of the order of 1800° to 1900° and vacuum of 10^{-6} Torr.

During the period under report, a few more systems involving yttrium oxychloride, cobalt chloride, rare earth sulphides, etc., have been studied.

(i) *Yttrium oxychloride:* Yttrium oxychloride was found to decompose completely at 1593°K. The decomposition study was carried out between 1188°K, and 1953°K, and $\Delta H°$, $\Delta S°$ and ΔCp values were obtained. They are 61·2 kilojoules/mole, −9·23 joules/mole deg. and 179 joules/mole deg. respectively.

Yttrium oxyfluoride was prepared from anhydrous YF_3 by thermal hydrolysis. Initially, YF_3 was obtained by precipitating it from aqueous $Y(NO_3)_3$ solution with aqueous HF. The precipitate was carefully washed and dried for 24 hours at 130°. Thermal hydrolysis of YF_3 was complete at about 500° only after a long time (120 hours). The high temperature dissociation of YOF is under study.

(ii) (a) *Vaporization of cobalt chloride* ($CoCl_2$)*:* The vaporization behaviour of cobalt chloride has been studied between the temperatures 953° to 1076°K. From the vaporization data obtained, the heat of sublimation gave a value of 53·87 Kcals., which was in good agreement with the third law value 52 Kcals.

(b) *Equilibrium reaction between* $Mn_3O_4(c)$ *and* $AlCl_3(g)$*:* Preliminary experiments on the reaction of $AlCl_3(g)$ with $Mn_3O_4(c)$ indicated the formation of manganese aluminate. However, the quantity of the spinel formed is very small. This may be due to the secondary reaction. The analysis of the reaction products suggests that the following reaction may be predominant:

$$Mn_3O_4(c) + 3AlCl_3(g) = Al_2O_3(c) + 3MnCl_2(g) + AlOCl(g) + Cl_2$$

The secondary reaction being :

$Mn_3O_4(c) + 3Al_2O_3(c) = 3MnAl_2O_4(c) + \frac{1}{2}O_2$. The reaction is being studied at temperatures 1200°-1450°K to understand its nature.

(iii) *Sulphides of some light lanthanons:* When light lanthanon (viz., La, Pr, Nd and Sm) sesquisulphides are heated in oxygen atmosphere, they form oxysulphates in the temperature range studied (500°-1000°), rather than sulphates and oxides. The kinetics of the reaction of $AlCl_3$ with light lanthanons are under investigation. $AlCl_3$ (vapour) reacts with lanthanum oxide at 850° to form lanthanum trichloride, lanthanum oxychloride, lanthanum aluminate and alumina. Lanthanum aluminate seems to be formed as a secondary reaction product between lanthana and alumina.

(iv) *Studies on the nature of high temperature reduction of different Indian ilmenite ores:* From the study of four samples obtained form Quilon (Kerala), Manavalakurichi (Tamil Nadu), Rajawadi and Malgund (Maharashtra), it was observed that the solid phase ilmenite ($FeO.TiO_2$-ferrous titanate) is more resistant to reduction roast as compared to ferric titanate ($Fe_2O_3.TiO_2$).

Ferrous titanate ($FeO.TiO_2$) and ferric titanate ($Fe_2O_3.TiO_2$) were synthesized. Both these compounds have been studied for their reduction behaviour. At optimum temperature of 1150°, iron oxide in these phases is reduced to the extent of 90% and 95% respectively.

Eventhough, iron oxide content of the ores and that of synthetic phases is preferentially reduced over titanium dioxide (TiO_2),it was observed that some TiO_2 got reduced to its lower oxides to the extent of 3% to 12%.

Chlorination studies have also been carried out on the mixture of the ore sample and carbon at various temperatures. At the optimum temperature of 600°, these ore samples are preferentially chlorinated for iron to the extent of 82%.

Preferential chlorination of synthetic phases is under study.

(v) (a) *Reaction of nickel chloride with cerium sesquisulphide* (Ce_2S_3)*:* The reaction of $NiCl_{2}(g)$ with solid cerium sesquisulphide (Ce_2S_3) was studied between 1227° and 1394°K employing flow technique. In addition to the complicated nature of the reaction, the side reaction $Ni(c) + NiCl_2 \rightleftharpoons 2NiCl(g)$ makes it very difficult to estimate the thermodynamic properties of the products of the reaction. The results, therefore, have been employed to understand the reaction stoichiometry which may be represented as:

$$Ce_2S_3(s) + 3NiCl_2(g) = 2CeCl_3(l) + 3Ni(c) + 1\tfrac{1}{2}S_2(g)$$

(b) *Reaction of* $NiCl_2(g)$ *with molten aluminium:* The reaction was studied between the temperatures 1290° and 1418°K. On the basis of the analysis of the gaseous products and the weight loss data the nature of the reaction has been studied. The stoichiometry can be written as:

$$NiCl_2(g) + 2Al(\ ) = 2AlCl(g) + Ni(c)$$

(vi) *High temperature vacuum microbalance:* The working of the vacuum microbalance unit has been tested and found satisfactory with regard to attainment of pressure 10^{-6} Torr at temperatures 800°-1800° necessary for the testing and measurement of certain chemical and physical properties viz., vaporizations etc., of refractory materials. The standardization of the balance assembly has been made with samples of silver of spectroscopic purity. The results obtained have been found consistent with the existing data given in the literature.

Vaporization studies on certain refractory metals and systems of ceramic materials in metal matrices are being attempted.

27. *Work on the synthesis and properties of new type glycol monoalkyl ethers for the control of water evaporation to extend the industrial utilization of cotton seed oil:* (SP-26/64)

The project was undertaken with a view to prepare fatty alcohols, the corresponding alkoxyethanols, propanols and butanols from cotton seed oil and to study the physical properties in bulk as well as monolayers on water substrate and to evaluate the water evaporation retardation property of these compounds.

It has been established that n-alkoxyethanols with the formula $C_n\text{-}OC_2H_4OH$ (n= 16, 18, 20, 22) were found to be superior water evaporation retardants as compared to the corresponding n-alcohols.

The method of preparation of the cetostearyl alcohol by high pressure hydrogenation of cotton seed oil was standardized. The n-alkoxyethanols, propanols and butanols containing C_{16} to C_{22} carbon atoms in the alkyl chain were prepared and evaluated as water evaporation retardants in the open air evaporimeters as well as in the wind tunnel in the laboratory by changing the wind speed and temperature. The physical properties such as surface viscosities, surface potential, π-A isotherms, specific resistance to water evaporation, rate of spreading, equilibrium film pressure and the collapse pressure of different monolayers were studied in order to evaluate the efficacy of these monolayers over water substrate.

During the last year, alkoxypropanols, $C_n\text{-}OC_3H_6OH$ (n = 16, 18, 20, 22) and two butanols viz., $C_n\text{-}OC_4H_8OH$ (n = 16, 18) of 99·9% purity were evaluated as water evaporation retardants both in the laboratory (petri dish experiments) and in semifield conditions (open air evaporimeter studies). It has been observed that oxy-propanols and oxy-butanols were found to be superior water evaporation retardants as compared to n-alcohols but were less efficacious than the corresponding oxy-ethanols.

A preliminary experiment on the physical properties such as π-A isotherms, rate of spreading (dN/dt) and equilibrium spreading pressure (π_e) were undertaken for a series of n-alkoxypropanols and butanols.

Surface viscosity, surface potential and π-A isotherms of mixed monolayers of n-alkoxyethanols and n-alcohols have been carried out to study the effect of intermolecular interaction, two dimensional phase transformations and orientation of the molecules for different pressures at 25°. All the mixed monolayers studied were found to be homogenous and miscible.

Surface tension measurements were continued for n-alkoxyethanols in the temperature range 45°-95°. From these data, relevant thermodynamic properties were calculated for understanding the nature of the surface region. Dielectric constant measurements were also continued for n-alkoxyethanols ($n = 16, 18, 20, 22$) at various frequencies and temperatures in order to detect the different phase modifications. These results have been compared with D.T.A. and X-ray studies.

The dielectric properties of a series of n-long chain alcohols (C_n-OH), alkoxyethanols C_n-OC_2H_4OH and propanols C_n-OC_3H_6OH ($n = 16, 18, 20, 22$) have been investigated in the frequency range of 0·5 Kcs. to 3 Mcs. between 25° to 100° both in the solid and the liquid states. All the above compounds exhibit polymorphic transformations in the solid state. These results have been confirmed by infrared spectral studies.

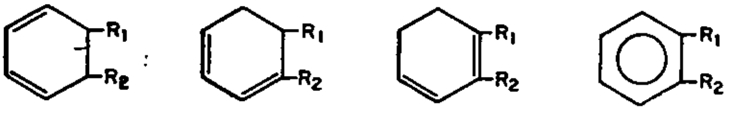
Excess enthalpy of mixing ($\triangle H_M$) of methyl-ethyl and butyl-cellosolve and carbitol with water were measured from 25° to 45°. $\triangle H_M$ values were found to decrease with increasing length of the alkyl chain and also with increasing temperature in both the series. The results indicate that the additional oxygen atom in the carbitols as compared with cellosolves is responsible for increased interaction of carbitols with water through hydrogen bonding with ether oxygen. The project is concluded.

28. *Investigation on the effect of heat on tung oil and derivatives of tung oil and the characterization and identification of compounds resulting from heat treatment to extend the utilization of tung oil:* (SP-29/63)

The investigations were undertaken mainly to study the thermal treatment of tung oil and its derivatives with a view to extend the utilization of this premier drying oil by the development of new industrial chemicals.

The five year project has been completed according to schedule (end of July, 1968) with gratifying success. Intramolecular thermal cyclization (targetted at the speciality industrial product, C_{18}-cyclic fatty acids) of recalcitrant eleostearate has been achieved in good yield (~60%) by the tactical use of sulphur as catalyst under optimized energetic conditions (240°/hour).

With the isolation of one more cyclic monomer and its spectrochemical characterization as methyl cycloeleostearate-III (3) and preparation of the *ar*-monomer (4) coupled with those [methyl cycloeleostearates-I (1) and II (2)] described earlier (Annual Report 1967-68, p. 13), the linear eleostearate-derived cyclic monomers are as follows:



(1) (2) (3) (4)

$R_1 = -(CH_2)_3CH_3$

$R_2 = -(CH_2)_7COOMe$

Sulphur-catalyzed thermal cyclization has been extended to the ω-hydroxy analogue of eleostearate (methyl kamloenate) a substrate of indigenous importance (accessible from Kamala seed oil, *Mallotus philippinensis*). The project is concluded.

29. *Wood phenolics with special reference to their use in chemotaxonomy and their biosynthesis by tissue culture studies:* (SP-28/66)

The phenolic constituents of wood play an important part in the technical utilization of wood. The object of the project is to isolate the phenolic constituents of certain woods, determine their structures, study the relation between the phenolics in leaves, cambium, phloem and xylem, investigate chemotaxonomic problems concerning woods, and examine the possibility of growing callus tissues of the plants under investigation and of using them for following biosynthesis of the phenolic constituents.

During the last two years, the heartwood and bark constituents of a large number of Indian plants have been examined. Eight species of *Artocarpus* have been examined and the presence of artocarpin and cycloartocarpin in all the species has been proved. Four *Morus* species have also been examined. From the bark of *M. alba*, four new analogues of artocarpin have been isolated and their structures established. The heartwood constituents have also been examined. Methods suitable for the isolation of individual phenolic compounds from complex extracts have been worked out. The bark constituents of some Indian pines have been examined and the presence of some flavone glycosides were noted for the first time. Two new novel biflavones were isolated from *Garcinia morella* and their structures established.

Since several phenolic compounds have been isolated from the heartwoods of many woody plants, it seems probable to trace out the possible biosynthetic pathways of some of these phenolics by using tissue culture as a tool. In view of the above, cultures of tissues of *A. heterophyllus*, *M. alba* and *T. grandis* were established and the tissues cultured on a large scale. The tissues do not seem to contain any known phenolics present in the respective trees. The tissues of teak contain an anthroquinone not present in the tree and its structure is under elucidation. The tissues of *A. heterophyllus* and *M. alba* also do not contain the same phenolics found in respective trees but contain different ones which are under isolation.

Work on the phenolic constituent of *M. alba* bark is being continued. Examination of the TLC of the acetone extract of the bark has indicated the presence of at least four compounds in addition to the compounds isolated earlier. Also an improved method for the separation of cyclomulberrochromene, cyclomulberrin, mulberrochromene and mulberrin has been worked out. This consists of countercurrent distribution (CCD) of the extract, first using chloroform: pet. ether: methanol: water system to separate the more polar constituents, which are again subjected to CCD using equal volumes of benzene: ethyl acetate: methanol: water system. Further purification of the various fractions by chromatography on silica gel and cellulose powder has afforded four new compounds in fairly pure form. The structures of these will be elucidated. Examination of the acetone extracts of *M. serrata* and *M. laevigata* by TLC has showed that these are similar to *M. alba.*

From the heartwood of *M. alba* resorcinol, β-resorcylaldehyde, resveratrol, oxyresveratrol, dihydrokaemferol, quercitin and dihydrooxyresveratrol have been isolated by CCD and chromatography on silica gel and cellulose powder. Dehydroxyresveratrol is isolated for the first time from a plant material.

The heartwood of *M. serrata* also gave results nearly the same as *M. alba*, however, dihydrooxyresveratrol was not noticed in this plant. The heartwood of *M. laevigata* also gave resorcinol, β-resorcylaldehyde, oxyresveratrol and two crystalline compounds which are not found to be present in the other two *Morus* species. The structures of these compounds will be elucidated.

The isolation of artocarpin, cycloartocarpin, artocarpesin and oxyresveratrol from *A. chaplasha* has already been reported. In addition, cycloarto-carpesin has been isolated from this plant. By using CCD and column chromatography resorcinol, β-resorcylaldehyde and resveratrol have also been isolated from this plant. Thus, it can be stated that a preliminary CCD is a valuable technique in separating individual compounds from complex plant extracts. This technique is also found helpful in simplifying thin layer and paper chromatograms.

A preliminary examination of the heartwood of *Taxus baccata* has now been completed, and a more thorough examination is under way. From the benzene extract the lignan secoisolariciresinol was isolated. From the acetone extract of the heartwood isotaxiresinol was isolated. Examination of the TLC of the acetone extract indicated the presence of a large number of other phenolics and these are being isolated.

In continuation of the work on the Indian pines, the bark of *Pinus insignis* was examined. This gave quercetin, taxifolin, catechin and 3, 4, 3′, 5′-tetrahydroxystilbene. The heartwood is being examined.

A detailed examination of the heartwood of *Castanopsis hystrix* was undertaken. From the acetone extract of the heartwood, gallic and ellagic acids were isolated. The acetone extract gave a large amount of solid which was insoluble in ethyl acetate and soluble in water. Over 80% of this solid was held up on a polyamide column and thus, appeares to be tannins. The nature of this solid is being investigated.

Work on *Garcinia* species is being continued. The bark of *G. morella* was extracted successively with benzene and acetone. From the benzene extract isomorellic acid and a new compound, m.p. 149°-150° was isolated. From the NMR and mass spectra this compound was identified as the reduction product of morellin in which the aldehyde group is replaced by the $-CH_2OH$ group.

From the bark of *G. xanthochymus*, morelloflavone and dihydromorelloflavone are isolated.

The structure of the latter was confirmed by alkaline hydrolysis and spectroscopic methods. The heartwoods of the *Garcinia* species are being investigated.

In addition to the work mentioned above, the heartwoods of *Pinus excelsa, P. insignis, P. longifolia, Picea morinda, Castanopsis indica, Juniperus macropoda* and *Aesculus indica* will be examined. Two species of *Nyssa* received from the U.S.A., will also be taken up for investigation.

⌑ ⌑ ⌑

PILOT PLANTS

1. *Aniline :* (PP - 4/63)

Aniline is an important organic intermediate required in the manufacture of drugs, rubber chemicals and explosives. This chemical is not presently manufactured in the country. The IVth Plan target for aniline is estimated at 9000 TPA. Hindustan Organic Chemicals Ltd., Rasayani, (HOC), will be producing 6000 TPA. At present about 4000 TPA of aniline valued at Rs. 95 lakhs is imported.

The process developed at the NCL is the continuous vapour phase catalytic reduction of nitrobenzene to aniline, using an indigenously developed catalyst. The scale of operation of the continuous pilot plant has been 5 kg./hr. HOC has agreed to consider putting up a 600 TPA aniline plant based on the NCL know-how mainly to assess the performance of the NCL catalyst on a large scale. Based on the NCL know-how, a turn-key proposal is being offered to HOC by a project engineering firm for the installation of the 600 TPA plant.

During the period under report, the continuous life test of the catalyst in a battery of reactors was carried out. A process for regeneration of the spent catalyst has been standardized. The catalyst quantity required per tonne of aniline produced has been correctly determined. A single tube reactor having the same diameter and height as in the large scale plant is now being run continuously at a rate of approximately 1 kg./hr. of aniline.

The dehydrating column for crude aniline was run continuously at a rate of 25 kg./hr. The pertinent data required for the design of 600 TPA plant were collected and passed on to the project engineers.

The process has been released to a project engineering firm on non-exclusive basis.

2. *Industrially useful products from polysaccharides :* (PP-2/58)

Work on this project had been initially oriented to investigate indigenous cellulosic raw materials for the manufacture of dissolving pulps of various grades and to develop processes for various cellulose derivatives. Imports of dissolving pulps during 1967-68 were of the order of 24,000 tonnes valued at Rs. 3·77 crores.

The scope of this project has been recently extended to include investigations on the manufacture of industrially useful products from polysaccharide materials available in the country.

During the course of last few years, processes for the production of high grade dissolving pulps from bamboo and *Eucalyptus hybrid* have been standardized.

During the year under review, five hardwood species from Maharashtra State were studied by prehydrolysis sulphate process. Pulps of high alpha-cellulose, low pentosan and acceptable D.P. values with low inorganic impurities have been obtained from all these species. Filtrability values of viscoses of some of the pulps are found good. Comparative study of mixed pulping of these species resulted in pulps of similar properties but with higher FZ values.

Eucalyptus hybrid up-graded pulps gave yarn of 2·8 to 3·5 g./denier strength and 14 to 15% elongation on tyre-cord spin-bath.

Commercial plastic manufacturing firms have tested cotton linters' pulp from NCL for use as plastic filler and their results are encouraging.

3. *Phthalates :* (PP-5/66)

Phthalates (Dioctyl, Dibutyl) are widely used as plasticizers for cellulose plastics, PVC, synthetic rubber, polythene, polystyrene and methylmethacrylate resins. The demand for phthalates in the coming years is estimated to be of the order of 18,000 TPA. Although a few firms are producing phthalates, some with foreign collaboration, large quantities are still imported. During 1967-68, 2840 tonnes of DOP and DBP valued at Rs. 81·6 lakhs have been imported.

Pilot plant trials to produce about 50-60 kg. per batch of phthalates have been successfully carried out, and the product so produced was evaluated by industry and found satisfactory.

The process has been released to two parties, one of which has already gone into production.

4. *Technical preparations of organic intermediates :* (PP-6/63)

There is a growing interest from the industry for developing know-how for the manufacture of a variety of organic chemicals and intermediates which are produced by batch processes and are imported in substantial quantities. Hence this multi-purpose project has been started wherein laboratory scale know-how is obtained and then scaled up suitably to collect the process and chemical engineering data necessary for commercializing the processes thus developed.

Pilot plant trials on the manufacture of *p*-nitrophenol, phenylacetic acid, phenoxyacetic acid, sopanox, etc., have been successfully carried out. Work is in progress for standardizing optimum conditions for the preparation of the following industrially important organic chemicals: triethylphosphate, trioctyl phosphate, triphenyl phosphate, trinonylphenyl phosphite, Simazine and salicylaldehyde.

5. *Fine Chemicals Project :* (PP-7/64)

The unit has been producing and selling fine chemicals routinely to various research organizations. With a view to make the project economically viable a sales promotion programme by way of advertisements and direct contacts with various parties, was undertaken and sales have been considerably boosted. In addition to the 325 chemicals described in the catalogue, many chemicals were custom-synthesized, noteworthy among these being 2-aminothiazoline, azodiisobutyronitrile, ethyl, methyl and phenyl isothiocyanates, *m*- and *p*-tolylenediamines, α-amino-β-naphthylthiazole and the 2-methyl substituted benzoxazoles, imidazoles and thiazoles.

Comparative figures of production and sales (in lakhs of rupees) for the past three years are given below:

Year	*Production*	*Sales*
1966-67	2·83	1·87
1967-68	2·08	1·46
1968-69	2·43	2·42

□ □ □

PRODUCT ORIENTED RESEARCH

1. *Cadmium sulphide photoconductive cells :* (ATT-2/66)

The cadmium sulphide cells (CdS) developed in this project have the property of changing their resistance when exposed to light. The change of resistance is large enough to make them sensitive to small changes in light intensity. Hence simple circuits can be designed which can be made to respond to such photo signals. Some of the important applications of such devices are in (i) automatic temperature control (ii) light sensitive relay (iii) industrial safety devices (iv) sound reproduction (v) camera exposure meters and (vi) scientific instruments.

Although the demand for this type of cells in the country is yet uncertain, it is likely that once the indigenous production is established there would be a sizeable demand for these cells for various devices.

The NCL process consists of the preparation of high purity cadmium sulphide, mixing it with suitable activators and firing it in a furnace. The CdS crystal plates are then suitably mounted and fixed to wire leads.

The optimization of condition for crystal growth has been carried out. A new furnace, incorporating improvements in design and for scaling up the preparation of the crystals, has been constructed. Measurements on conductivity, photocurrent and response time have been continued. The techniques of encapsulation and mounting etc., have been finalised.

An informative note consisting of its specifications and applications, along with typical circuit, has been circulated to parties in the electronic industry. More than a dozen parties have shown interest in the product to whom free photocell samples have been supplied earlier for evaluation. Reports from these parties show that the cells compare well with similar imported samples.

Based on the photocell, an automatic general photo relay has been developed to demonstrate the utility of the photocell.

The process has been released to a party on non-exclusive basis.

2. *Tin oxide resistor :* (ATT-61/68)

As high temperature and high voltage resistors, thin films of tin oxide have great potential in the electronic industry. Demand for these resistors is growing with the development of the defence electronic industry, where these are mainly used for their rugged construction and stable performance.

A number of processes for deposition of electrically conducting tin oxide films on glass and ceramic substrates have been studied. Preliminary runs with an improved rotary furnace have been completed. It has been found that tenacious tin oxide coatings giving required values of resistance can be deposited on ceramic substrates. A modified furnace has been constructed and is under installation.

A study of the conductivity and mobility behaviour of the tin oxide deposits on glass and ceramic substrates is in progress. A special vacuum cryostat for carrying out these studies at low temperature has been constructed and satisfactorily tested.

The data obtained from these measurements will be useful to optimize production parameters.

3. *Ferroelectric materials :* (AB-2/57)

In recent years ferroelectric ceramics are commercially used in phonograph pickups, ultrasonic transducers for high power generation, ceramic wave filters and memory and display devices. In India there exists a potential market for this material and for the devices made out of it.

The investigation is aimed at the preparation of ferroelectric ceramics suitable for the above applications and their structural, dielectric and other properties in relation to their ferroelectric and associated piezoelectric properties are being studied.

Doped lead titanate ceramics of the general formula

$$\mathrm{Pb}\left[\mathrm{La}_{0\cdot5}\left(\mathrm{B}_{\mathrm{II}}^{\;5+}\right)_{0\cdot5}\right]_{x}\mathrm{Ti}_{1\text{-}x}\mathrm{O}_{3}\quad\text{where } \mathrm{B}_{\mathrm{II}} = \mathrm{Nb} \text{ or } \mathrm{V}$$

were prepared and the various properties studied. In order to improve the properties of these ferroelectric materials in respect of dielectric constant and electromechanical coupling coefficient, so that they can be effectively used for phonograph pickups etc., doping with WO_3, MnO_2, SrO, etc., has been tried. It has been found that by partially substituting Pb with Sr, spontaneous polarisation of the material can be considerably increased.

4. *Posistors :* (ATT-62/68

The object of this investigation is to develop new compositions of posistor material showing PTCR (Positive temperature coefficient of resistivity) behaviour. Posistors are used in electronic and electrical applications such as temperature indicator, no-contact switch, temperature controller, timing devices and for the purpose of thermal protections.

Based on $BaTiO_3$ doped with oxides of rare earths, thermistor compositions exhibiting high values of αmax., (positive temperature coefficient of resistivity) have been developed. These are pressed into forms of pellets and then sintered. The temperature/resistance characteristics of these products are being studied in detail.

New systems doped with other suitable metal oxides have been prepared on laboratory scale and their properties are being studied.

5. *Polycrystalline silicon :* (ATT-9/67)

Silicon diodes and transistors are being used in large quantities in the country. Several firms have already established production of these silicon devices from the imported raw materials. It is estimated that about 500 kg. (value Rs. 15 lakhs) of polycrystalline silicon are imported per year.

The unit for the preparation of trichlorosilane, has been run successfully and the optimization of process variables such as H_2:Cl_2 ratio, rate of feed gas, temperature of the reactor and catalyst has been carried out. This batch process can now yield about 4-5 litres trichlorosilane per run at the rate of 500 ml./hr. A unit for the purification of this intermediate by fractional distillation has been set up.

The laboratory unit for the reduction of trichlorosilane to silicon (50-100 g. /run of 30-40 hr.) has also been run successfully several times. Data on the effect of H_2:$SiHCl_3$ ratio, temperature of the trichlorosilane bath, the furnace temperature and the rate of input of the reactants have been obtained.

6. *Ferrite compositions:* (ATT-10/59)

Hard ferrites find wide applications in cycle dynamos, loudspeaker magnets, latching magnets, motors, etc. They are less susceptible to demagnetizing influence and temperature effects. Hard ferrites are not known to be produced in the country at present although internal requirement by 1974 is estimated to be of the order of 100 TPA valued at Rs. 20 lakhs.

The NCL process for hard ferrites has now been released to a firm, and with the active help of NCL scientists trial runs of hard ferrites under industrial conditions have been undertaken.

Soft ferrites are ceramic magnetic materials which are extensively used for the manufacture of high frequency cores, radio antenna rods, H. F. chokes and for many other electrical and electronic devices. Soft ferrities are being produced in the country by a few firms but their present production is far short of the country's requirement. According to Bhabha Committee report, requirement of soft ferrites is estimated at 117 TPA valued at about Rs. 1·17 crores.

A soft ferrite composition comprising of minor beneficial additives has been prepared on 1 kg./batch scale and samples in the form of antenna rods and toroids have been made. The process variables had to be reoptimized to get the best samples. Antenna rods made from one of these compositions are found suitable for high frequency application (upto 18 mc/sec.).

Experiments on the orientation of the magnetic materials have been initiated. The value of $(B \times H)_{max}$ obtained so far is in the range of $(2{\cdot}6\text{-}3{\cdot}0) \times 10^6$ gauss × oerst.

7. *Potential catalyst materials :* (AB-8/67)

Catalysts are specific materials having cardinal importance in chemical industry. Work has been undertaken on industrially important potential catalyst materials.

7·1 *Alumina:* Alumina is a well-known catalyst used in many synthetic organic reactions. The catalytic properties of alumina are specific and depend upon the mode of preparation and activation temperature. With a view to study the correlation between the physical properties of the catalyst and the activation temperature, alumina was precipitated at pH 8 and was activated at different temperatures.

The thermogravimetric studies of alumina under vacuum and in air showed that the dehydration occurred in one step between 200°-250° and 250°-300° respectively. The surface areas of alumina activated at different temperatures showed sharp increase in the specific surface from 50m^2/g. to 435 m^2/g. between 200° and 500° while on further increase in activation temperature from 500°-1000°, the surface area showed a gradual decrease from 435 m^2/g. to 75 m^2/g. These results are in accord with the observation that the catalytic activity of alumina is reduced by activating above 500°.

The activation of alumina under vacuum as well as its sintering properties at 500° have also been investigated.

7·2 *Molecular sieves:* Crystalline aluminosilicates (molecular sieves) have recently gained importance as selective adsorbents and catalysts for a variety of reactions such as cracking, dehydration, alkylation, condensation, amination, etc. Work has been undertaken to prepare this type of molecular sieve catalysts and their catalytic reactions of industrial importance will be studied.

A few trial experiments have been conducted for the development of the know-how for preparing the molecular sieves using sodium silicate and sodium aluminate.

8. *Silicones and silicone intermediates* : (ATT-13/66)

According to a five year programme of research and development on silicone products, work on the preparation of monomers and intermediates has been undertaken at this laboratory.

Some estimates on the expanding demand of silicones in India are available. The present total requirement of silicone products is around 100 tonnes annually which is likely to double itself in five or six years. Their average bulk price is in the range of Rs. 30-35/kg., but prices vary for different products. Average siloxane content of the silicone products is around 60 to 70 per cent. It will be seen that the country's requirement still falls far short of an economic unit for the manufacture of dimethyl dichlorosilane by fractionation (200 theoretical plates) of Rochow chlorosilane mixture; which provides scope under Indian conditions for examining alternative methods of processing the Rochow mixture to obtain pure dimethyl and other siloxanes.

The Rochow reaction has been under study during the year for laboratory optimization. With an agitated bed and a fairly careful temperature control, there was little difficulty in obtaining good conversion yields based on methyl chloride (upto 86%). However, to obtain a high percentage of the Me_2SiCl_2 in the liquid product has presented much greater difficulty, not the least of which is a quick and fairly accurate method of estimating it in the liquid mixture. Present status of the investigation indicates that higher values of the Me_2SiCl_2 in the liquid product can be attained only at a partial sacrifice of the total liquid yield calculated on methyl chloride. This would make a recirculation of the MeCl gas compulsory in any commercial unit of production. So far the Rochow liquid (mixture of the chlorosilanes) has been produced at the rate of about 40 g./hr. from a charge of 200 g. of silicon powder (from ferrosilicon) in a vertical glass reactor of 4 cm. internal diameter. A larger unit, expected to yield about 0·5-1 kg. per hour of the liquid is under fabrication.

Ordinary fractional distillation of the chlorosilane mixture gives a fraction which is essentially a mixture of Me_2SiCl_2 and $MeSiCl_3$. This is of little use as such, and a separation of these two liquids is necessary. As an alternative to fractional distillation of these highly moisture-sensitive chlorosilanes, the Laboratory is working on a process of separation through their conversion to other derivatives and isolation of the dimethyl siloxane low polymer, an equally suitable intermediate for polymerization to silicones. In addition, a process for converting methyl trichlorosilane, a major bye-product of Rochow reaction, into phenyl methyl siloxane by Grignard synthesis with chlorobenzene is being developed.

A silicone fluid rain repellent, used on aircraft windscreens, was identified and synthesized on an enquiry from the Ministry of Defence.

9. *Ethyl silicate :* (ATT-120/68)

Ethyl silicate of 40% silica content is a light coloured liquid of low volatility used mainly for precision casting of high melting alloys. Its other uses, e.g., as a pigment binder for paints and surface hardener for sandstones, have also been mentioned. Figures are not available on the country's requirements, but it is known that the product is wholly imported at present.

Raw materials required are ethyl alcohol and silicon tetrachloride. A unit for producing 1 kg. of silicon tetrachloride per hour from indigenous ferrosilicon has already been reported from this Laboratory (Annual Report 1966-67, p. 25). A laboratory batch process for making ethyl silicate of the above specifications, producing 200 g. of the liquid per batch has now been worked out. The Laboratory is in touch with some metal engineering industries to assess further scope for development of the process.

10. *Burning of $TiCl_4$ in oxygen to produce rutile titania :* (ATT-65/68)

Pigment grade TiO_2 is manufactured (18 tonnes/day) in India by a firm in Kerala from Indian ilmenite following a conventional sulphate route which is a multistage batch process. The titania obtained in this process is the anatase form and is not easily converted to rutile grade on calcination. A more modern process for the production of pigment titania is the chloride process. In this, the titania-bearing material is chlorinated at elevated temperatures to obtain anhydrous $TiCl_4$ which after purification is burnt in oxygen to oxide. The product is mostly rutile form and is superior to the anatase in whiteness and covering properties. Rutile titania is not, at present, produced in the country and is imported to the tune of 2000 TPA valued at about Rs. 64 lakhs.

The laboratory unit comprising a $TiCl_4$ feed mechanism, nickel burner, refractory reactor and refractory lined cyclone, has been successfully used to carry out the oxidation of $TiCl_4$ at temperatures ranging from 1200° to above 1700°. Analysis from various sampling points shows a variation of the adsorbed chlorine content from 0·05% to 19·0%. Work is in progress to minimise the adsorption of chlorine and to get an uniform product. By controlling the flame temperature and the rate of feed of $TiCl_4$ vapour, a predominantly rutile product has been obtained. To obtain completely rutile product, addition of anhydrous aluminium chloride along with the vapours of $TiCl_4$ is being studied. Microscopic examination of the product showed that product is in the form of easily dispersible agglomerates of 2-3 micron size. To determine the ultimate particle size and shape, the product will be examined by electron microscope.

It has been observed that visual method of comparison of X-ray powder pattern of anatase, rutile and their mixtures, gives reproducible results only when content of one of the constituents is very high.

11. *Polytetrafluoroethylene :* (AB-46/68)

Polytetrafluoroethylene (PTFE) is a heat and corrosion resistant polymer extensively used in the manufacture of gaskets, coatings, linings, frictionless bearings, etc. At present this is not produced in the country and is imported to the value of Rs. 1 crore per year.

The preparation of PTFE consists of two steps:

(a) Pyrolysis of Freon 22 (dichlorodifluoromethane) to yield tetrafluoroethylene (TFE).

(b) Polymerization of TFE at high pressures in presence of water, catalyst such as free radical initiators and other additives.

As reported earlier the first step had been worked out in some detail and the conditions of pyrolysis optimized. The pyrolysis assembly is being run to provide TFE for the ploymerization studies.

Polymerization study was carried out in an electrically heated 500 ml. rocker shaker autoclave capable of withstanding 1000 atm. A pressure vessel designed to stand 250 psi. was fabricated and used to optimize reaction parameters such as water/TFE, catalyst/TFE ratios and amount of additive, amount of inhibitor, pressure, temperature, time etc.

Under suitable conditions ivory white granules or a fine white powder of PTFE was obtained, the amounts, however, being small due to low capacity of autoclave and low pressure available from the booster used. Based on the data collected, suitable improvements are being made to improve the yields of PTFE.

12. *Butyl titanate :* (ATT-95/67)

Butyl titanate is an additive used in insulating varnishes and in rust proofing, waterproofing and fire proofing paints. It also finds applications as a catalyst in some polymerization reactions. Butyl titanate is not manufactured in the country and its requirements are met by imports. Demand of butyl titanate is estimated to be 20 TPA valued at Rs. 4 lakhs.

All raw materials except titanium tetrachloride are at present available indigenously, however titanium tetrachloride is likely to be available in the near future when M/s. Travancore Titanium Products Ltd., Trivandrum, will start utilizing the NCL know-how for its commercial production.

A batch process has been standardized on 10 kg. scale with 90% yield of butyl titanate.

The process is available for release.

13. *Utilization of some mineral concentrates :* (ATT-66/68)

The Sikkim Mining Corporation produces annually Rs. 20 lakhs worth of mineral concentrates containing copper, zinc and lead. At the instance of the Corporation, preliminary work on the recoveries of these metals from their concentrates was done. Conventional roasting leading to the oxidation of the concentrates to sulphates (Table I) and leachings with sulphuric acid and brine were carried out. It was found that the recovery of zinc and copper with dilute H_2SO_4 were 70 and 56 percent respectively, while recovery of lead (with saturated brine and dilute acid) was 51% only.

TABLE I

SULPHUR CONTENT IN THE CONCENTRATES CALCINED AT VARIOUS TEMPERATURES

	Copper concentrate			*Zinc concentrate*			*Lead concentrate*
	450°	540°	570°	500°	600°	800°	600°
Total sulphur %	14·3	11·54	15·05	—	13·9	6·13	17·2
Sulphide sulphur %	—	<0·50	<0·50	<0·40	<0·50	<0·50	<0·50

The laboratory data obtained by utilizing fluidized-bed roasting technique showed no particular advantage over the conventional roasting in the recoveries of zinc and copper. However, lead recovery was improved considerably (80%) by this technique. Factors like temperature and time which would influence the recoveries of the metals were also studied.

A few experiments were also carried out on direct pressure leaching of the zinc concentrate with sulphuric acid and oxygen under pressure. In this process, roasting is eliminated and sulphur recovered as elemental sulphur.

A mild-steel lead-lined reactor with external electrical heating (150°) and equipped with stirring arrangement was fabricated. Commercial oxygen was supplied through suitable pressure reducing control valves. About 80% zinc was recovered from the zinc concentrate. In one experiment (35 psi. O_2 partial pressure), besides the free sulphur present in the pellets, some quantity of free sulphur associated (colloidal form) with leach solution was also recovered. In a trial experiment with copper concentrate, the leach solution contained almost the entire zinc present in the concentrate (recovery of zinc 96%). Due to the leakage of the reactor through its glands, further work will be carried out on fabricating a proper reactor.

14. *Preparation of magnesium and magnesium calcium silicate for thermal insulation :* (ATT-67/68)

Last year on behalf of a private firm, work on the preparation of thermal insulation blocks of calcium silicate was conducted and the party has started manufacture of these thermal insulators on a scale of 2 tons/day of calcium silicate by a process developed in this Laboratory. Thermal insulators based on calcium silicate can stand temperatures upto about 600°-650°. Since magnesium silicate is capable of withstanding much higher temperatures (more than 1000°), work on standardizing a process for the preparation of suitable type of magnesium silicate has been undertaken.

Several compositions of magnesium silicates, viz., di, tri, meta and tetra silicates were prepared and it was found that as the silica ratio increases, the bulk density of the material decreases. Sample of meta-silicate prepared by the same method although showed the same analytical composition, varied in their bulk densities. The bulk densities of the products were of the order of 10 lbs./cft. Moulds prepared with some of these samples along with lime, ammosite and alum were found to have a bulk density of the order of 20-30 lbs./cft. and good strength. However, there was considerable shrinkage of the blocks in most of the cases. Hence, it was concluded that magnesium silicate for high temperature insulations can be used only as powder. In view of the lack of techno-economical data, further work will only be taken up if some party shows interest in exploiting the process.

15. *Chromatographic adsorbents and other chemicals* : (ATT-14/4)

Less frequently used chromatographic adsorbents such as calcium carbonate, calcium hydrogen phosphate, magnesium oxide and magnesium trisilicate have been prepared to meet small requirements of various firms at the FCP. Titanium trichloride solution was also prepared to meet the demand of some research institutes.

16. *Aluminium silicate as rubber filler :* (ATT-121/69)

Aluminium silicate having about 70% silica content, low bulk density and high purity is used as a rubber and plastic filler. A few experiments to prepare this product have been carried out with encouraging results.

17. *Aluminium hydroxide gel :* (ATT-122/69)

Indian Veterinary Research Institute, Kumaon, (UP), is at present importing this chemical under the trade name 'Alhydrogel'. The demand of the above Institute is nearly 100 TPA valued at about Rs. 10 lakhs. Preliminary attempts have been made to prepare the gel starting from indigenous chemicals.

18. *Di-o-tolylbiguaniden :* (ATT-22/66)

This chemical is used as an antioxidant for soaps and other cosmetics under the commercial name 'Sopanox'.

The pilot plant investigations regarding the process details were completed. At the request of the entrepreneur who offered to purchase the process, larger pilot plant runs have been taken in connection with commercial production of the chemical. These runs have been concluded and one tonne of the product sold to the party. The process is being released.

19. *Dyes for synthetic fibres :* (ATT-23/66)

Work on the dyes for synthetic fibres was continued. The application of dyes synthesized earlier to three typical synthetic fibres (polyester, nylon and secondary acetates) was investigated. Usual disperse dyeing procedures were employed for nylon and secondary acetate, but for the polyester both carrier dyeing and high temperature dyeing methods were tried. Majority of the dyes showed moderate to good affinity for polyester fibres and fair to poor affinity for nylon and secondary acetate. Light washing and rubbing fastness were moderate to good; gas fading tests are under study. The possibility of commercial exploitation of these results is being considered. A patent application to cover the preparation of these dyes has been filed (I.P. 116453).

Larger scale (1kg./batch) preparation of a few dyes selected from earlier work was carried out to get enough sample for mill trials. Two dyes were sent to a textile mill for extensive testing on bulk dyeing of synthetic fibres. The results are encouraging from the point of view of affinity, build-up characteristics, levelling, reserve on other fibres, dispersability and fastness roperties. A party has offered to purchase the patent rights and the process for commercial exploitation.

20. *Technical preparations of organophosphorus compounds :*

20·1 *Triethyl phosphate :* (ATT-24/66)—Triethyl phosphate is used as a catalyst in the manufacture of ketene from acetic acid. It finds use as a plasticizer for cellulose plastics, a non-corrosive solvent, as a starting material in the manufacture of insecticides and as an additive to petroleum and lubricants. Triethyl phosphate is at present imported and current requirements are estimated at about 50 TPA valued at Rs. 6 lakhs.

Based on the reaction of phosphorus oxychloride on sodium ethoxide in absolute alcohol, a laboratory scale process was standardized. During the bench scale experiments (2 kg./batch) it was thought of introducing certain modifications in reaction conditions etc. Accordingly the laboratory scale procedure has been modified. Based on these modified parameters, pilot plant experiments are being carried out. The process is offered for commercial release.

20·2 *Tris-nonylphenyl phosphite :* (ATT-71/67)—Tris-nonylphenyl phosphite (TNPP) is a superior stabilizer for G.R.S. polymer and white rubber. It is non-discolouring and imparts less odour to the finished polymer. It is resistant to hydrolysis and hence, could be added to latex as an aqueous emulsion. The chemical is sold in U.S.A., under the trade name 'Polygard'. At present it is entirely imported to the tune of 70 TPA valued at Rs. 10·5 lakhs.

The laboratory process has been scaled up and batch sizes upto 150 kg. have been taken in pilot plant trials. The sample obtained in over 95% yield is of a satisfactory quality as per specifications for the commercial product. The sample also passed the tests for its anti-oxidant and anti-discolouring properties. The product was sent to two firms for consumer acceptability trials and their reports are awaited. The process is available for commercial exploitation.

20·3 *Trioctyl phosphate :* (ATT-119/68)—Trioctyl phosphate is used as a low temperature plasticizer for polyvinyl chloride-type resins, especially when flame retardance and fungus resistance are required. It is compatible with nitro-cellulose, ethyl cellulose, polystyrene and chlorinated rubber.

Starting from 2-ethyl hexanol and phosphorus oxychloride an average yield of 90-92% of tri-(2-ethylhexyl) phosphate has been obtained on laboratory scale. The sample was found to meet the specifications (colour, refractive index, viscosity and acidity etc.,) of a commercial product.

Following bench scale experiments, a few pilot plant trials (12 kg./batch) were successfully carried out.

20·4 *Triphenyl phosphate:* (ATT-125/68) — Triphenyl phosphate (TPP) is an important plasticizer for photographic films and, is at present, imported by the Hindustan Photo Films, Ootacamund.

The laboratory scale (250 g./ batch) preparation of this product was investigated and yields around 93-95% based on phenol, have been obtained. Experiments are in progress to standardize optimum conditions for a product meeting the rigid specifications desired by the industry. Several experiments have been carried out and the product standardization is in progress.

21. *Simazine :* (ATT-126/68)

Simazine is a herbicide useful in controlling herbs associated with wheat, corn and other crops. It is a cyanuric chloride derivative obtained by the condensation of two moles of monoethylamine with one mole of cyanuric chloride. The technical preparation has been standardized on the bench scale (0·5 kg./batch) and a few batches have also been taken. The sample has been sent to a commercial firm for dilution and standardization to produce wettable powder for field trials. The results are awaited.

22. *Hydroxyethylstarch :* (AB-60/68)

For the preparation of hydroxyethylstarch (HES) as a plasma expander, starch containing mainly amylopectin (>95%) is required. This type of starch is obtained from waxy maize which is a special variety cultivated in the United States. Hence, it has been decided to prepare HES required for textile industries.

The literature survey indicates that HES prepared from total starch and ethylene oxide has wide applications. These hydroxyethyl starches are also available in different varieties depending upon their DS (degree of substitution). Enquiries made with several industrialists in the country indicated that HES may compete with maize starch, if the cost factor is favourable.

HES of different DS have been prepared from total corn starch and ethylene oxide. Samples (1 kg. each) have been sent to a few textile mills for testing as a starch substitute. The results are awaited.

23. *Saccharification of cellulose :* (AB-22/67)

This work was undertaken with a view to study the possible economic production of D-glucose by saccharification of cellulosic agricultural wastes.

In the initial experiments, the yield of D-glucose obtained from ground nut shell pulp by the action of hydrochloric acid was 55 to 62%. A method has been developed in which the yield of D-glucose from groundnut shell pulp has been considerably improved by a combined action of hydrogen chloride and hydrochloric acid. The reaction conditions under which these high yields were obtained are being studied in detail.

24. *Cellulose powder :* (ATT-112/68)

In the course of studies in the saccharification of cellulosic agricultural wastes, the unreacted cellulose was recovered as a fine powder under certain conditions. A substantial amount (nearly 800 TPA) of cellulose powder of different grades is being imported for use as a filler in thermosetting plastic powders and in rubber as well as for coating for welding electrodes. Special types of cellulose powder are also used in chromatography.

In view of this, a detailed study was made for the preparation of different types of cellulose powder starting from various cellulosic materials. A method has been developed to prepare cellulose powder of >300 mesh size, from cotton waste and groundnut shell pulps.

25. *Synthetic glycosides and other synthetic carbohydrate materials:* (ATT-19/66)

25·1 *Glycosides and thioglycosides :* A number of glycosides and thioglycosides are important for studies in genetics. These glycosides are costly and preparation of many of them has not been described in literature. Some of these glycosides and thioglycosides have been prepared and exported to U.S.A. and sold to some institutes in India.

During the period under report, six different glycosides have been sold to research institutes in U.S.A., and India:

1. Phenyl-β-D-galactopyranoside
2. Phenyl- ∝-D-galactopyranoside
3. Phenyl-β-D-thiogalactopyranoside
4. Phenyl- ∝-D-thiogalactopyranoside
5. *o*-Nitrophenyl-β-D-thiogalactopyranoside
6. *o*-Nitrophenyl- ∝-D-thiogalactopyranoside

25·2 *Phenolphthalein-D-glucuronide :* This is a costly and rare chemical sold at a price of about Rs. 700-1000/g. It is used for estimating glucosidase activity of enzymes and is usually prepared by a biochemical process. Work on the synthesis of this compound, according to the method available in literature, was undertaken starting from D-glucurone, the intermediary steps for the preparation of methyl D-glucuronate and methyl 1, 2, 3, 4-tetra-*o*-acetyl-D-glucuronate have been standardized.

26. *N-Acetylneuraminic acid :* (ATT-113/68)

This carbohydrate derivative is an important and costly biochemical selling at about Rs. 1000/g. The Biochemical Unit of the CSIR, New Delhi, has indicated that about Rs. 1 lakh worth of this chemical could be exported per year. It is usually used for estimation of enzyme activity and is prepared by biochemical methods, but synthetic approaches have also been worked out recently.

The work on the synthesis of this compound has been undertaken. Starting from D-arabinose, the steps involving the Sowden-Fischer nitromethane synthesis have been standardized for the preparation of the key intermediate 1-nitro-2-acetamido-1, 2-dideoxy-D-mannitol.

27. *Substitute for gum arabic :* (ATT-107/66)

This work was undertaken initially at the instance of the Post and Telegraphs Board, New Delhi, to develop an indigenous substitute for the imported gum arabic.

In addition to its use as an adhesive, gum arabic finds extensive uses in textile processing and printing, and in food and pharmaceutical industries. More than Rs. 50 lakhs worth of gum arabic is annually imported in the country.

A process was developed earlier for the modification of an indigenous gum (Ghatti) available in abundance, to a product having adhesive properties comparable with those of gum arabic. This process, after slight modifications, has been scaled up in batch sizes of 20 kg. Large samples of the modified gum from these batches have been sent to five different interested parties for testing and evaluation. Their reports are awaited. Considering these reports, the process will be released for commercial exploitation.

A vegetable gum known as 'Ain' gum is available in fairly large quantities in many parts of the country, but does not find much use. Investigations on the structure of this gum were undertaken with a view to find whether its structure could be suitably modified to obtain a product having useful properties such as those of gum arabic. The structure of the gum had been determined and reported earlier. Unlike gum arabic in which the backbone is a D-galactan chain, Ain gum has a backbone constituted of D-galactose and D-glucuronic acid combination. In gum arabic, D-glucuronic acid is present in the branching units only. Moreover, Ain gum has D-xylan branches which are entirely absent in gum arabic.

Attempts to modify Ain gum to a product having properties similar to those of gum arabic, therefore, proved unsuccessful.

28. *Cashewnut shell gum :* (ATT-127/69)

Cashewnut shells contain a water soluble polysaccharide (CNS gum) to the extent of about 10%. Conditions for isolation of the polysaccharide (CNS gum) in good yield from the aqueous extract of cashewnut shells of different origin (such as natural shells, spent shells, oil-free shells etc.,) have been standardized. Further work on the evaluation of this gum is undertaken.

29. *Vitamin B_6 :* (ATT-16/66)

Vitamin B_6 is not manufactured in the country and is imported to the tune of 6000 kg./annum valued at Rs. 11 lakhs.

Earlier, a ten-step synthesis starting from chloroacetic acid was standardized. However, a study of recent developments in this synthesis by different routes revealed that a five-step process from *dl*-alanine is more promising.

Accordingly, work on synthesis of pyridoxine from *dl*-alanine was undertaken. During the period under report, the first two steps of the synthesis through ethyl-*dl*-alaninate hydrochloride and its N-formyl derivative have been optimized. The preparation of the key intermediate 4-methyl-5-ethoxyoxazole (third step) has also been obtained in good yield. Further work to improve the yields in this step is in progress.

Exploratory experiments on the fourth step product, i.e., 2-methyl-3-hydroxy-4, 5-dicarbethoxypyridine hydrochloride have also been undertaken.

30. *N, N-Diethyl-meta-toluamide :* (ATT-18/65)

The compound is widely known to be an effective mosquito repellent. At present this chemical is not produced in the country. Information about its imports or requirements etc., is not available. Defence department is interested in this chemical.

The technical preparation consisting of catalytic oxidation of commercial xylene and condensing the mixture of toluic acids, so obtained, with diethylamine is being standardized. Attempts to recycle the recovered catalyst and to optimize the yields of the final product are in progress. Earlier, a product containing approximately 70% diethyl-*m*-toluamide was sent to AFMC, Poona, for field trials. The product was found satisfactory in these tests.

31. *Colchicine :* (ATT-68/68)

The current annual demand for colchicine, which is valuable both in pharmacy and plant breeding, is approximately 2 kg. valued at Rs. 70,000. The demand for the year 1970-71 is expected to be almost double the amount. Colchicine may also have a good export potential.

Colchicine-type alkaloids present in the tubers of *Gloriosa superba* (grown in Poona area) and in the corms of *Colchicum luteum*, have been separated and characterized. The variation in the percentage of the above alkaloids with the age of tubers (*Gloriosa superba*) was studied. Colchicine was found to be a minor constituent alkaloid in these tubers.

Other sources supposed to be rich in colchicine are under investigation.

32. *Terpin hydrate and terpineol:* (ATT-69/68)

Terpin hydrate is mainly used as an expectorant in cough mixtures, while terpineol having a sweet lilac odour is largely consumed in the perfumery industry. There is no regular production of these chemicals in the country. The total import of terpineol and related products is estimated to be of the order of 200 TPA valued at Rs. 10 lakhs.

The preparation of terpin hydrate by the hydration of α-pinene has been standardized on 500 g./batch scale. α-Pinene is available from Indian turpentine oil. Further work on standardizing the preparation of terpineol from terpin hydrate is in progress.

33. *Allantoin :* (AB-52/68)

Allantoin is glyoxyldiureide. This drug is used to stimulate cell proliferation in ulcers, non-healing wounds, fistulas etc. The powder is generally applied by dusting or in the form of an ointment.

Based on the reaction between dichloroacetic acid and urea, laboratory scale preparation was carried out. The product was tested by the firm which initiated this work and was found to conform to their specifications.

Further work on standardizing the technical preparation will be undertaken if some party is interested in commercializing the process.

34. *p-Nitrophenol :* (ATT-73/67)

p-Nitrophenol is mainly used for the production of pesticides. It is also used in the preparation of *p*-acetamol, an antipyretic drug. Estimated demand of *p*-nitrophenol for parathion manufacture alone is of the order of 300 TPA. Although it is manufactured by a few firms in the country, imports of *p*-nitrophenol during 1967-68 were of the order of 190 tonnes valued at Rs. 9·7 lakhs.

The laboratory scale preparation of *p*-nitrophenol by the alkali fusion of *p*-nitrochlorobenzene (750 g. / batch) has been standardized. Yield of about 95% *p*-nitrophenol (purity 97-98%) has been obtained. Further scale up work is in progress. The process is available for release.

35. *p-Acetylsulphanyl chloride :* (ATT-72/67)

p-Acetylsulphanyl chloride (ASC) is an important intermediate in sulpha drug manufacture. It is prepared technically by the chlorosulphonation of acetanilide using an excess of chlorosulphonic acid. The study was undertaken to (i) make a stable ASC in good yields, (ii) check the stability of the product, and (iii) recover sulphuric acid of suitable concentration.

An experimental method was developed on the laboratory scale to produce ASC (70% yield). The product assayed, during the first week after preparation, showed 95-98% purity, but deteriorated to about 80% ASC in three months. The project is abandoned.

36. *19-Norsteroids and other modified steroids :* (ATT-30/67)

19-Norsteroids of anabolic and antifertility activity are gaining considerable importance in medicinal products. A number of approaches for the preparation of $\Delta^{1,4,6}$-triene-3-ones and $\Delta^{1,4}$-diene-3-ones of the cholestane and spirostane series have been carefully examined.

The dienone-phenol rearrangement of the trienones and the reductive aromatization of dienones have been studied and 3 α, 12 α-diacetoxy-Δ^{22}-24-norcholene, a potential intermediate for the preparation of estrone, has been prepared in very good yields from cholic acid through oxidative decarboxylation with lead tetraacetate in the presence of cupric acetate.

Further work on standardization of the process will be undertaken if some party shows interest in its commercial exploitation.

37. *Preparation of photosensitive chemicals :* (ATT-76/68)

The project has been undertaken with the object of standardizing technical preparations of the following two photosensitive chemicals: (i) 2, 3-dihydroxynaphthalene-6-sulphonic acid, and (ii) light sensitive stabilized diazonium salts. Both these chemicals are used for the preparation of photosentitive papers and are not manufactured in the country. Compound (i) is imported to the tune of 3 TPA valued at Rs. 1·5 lakhs; Compound (ii) is also imported to the same extent.

37·1 *2:3-Dihydroxynaphthalene-6-sulphonic acid:* Experimental conditions have been standardized on the batch size of 1 kg. for the preparation of sodium salt of the above compound (i) by alkali fusion of crude R-salt, in satisfactory yield and purity. Sample has been sent to industry for evaluation.

37·2 *Light sensitive stabilized diazonium salts :* Starting from N-β-hydroxyethyl-N-ethylaniline the *p*-amino-N-β-hydroxyethyl-N-ethylaniline has been prepared by nitrosation followed by reduction. The resulting aniline was diazotized and its zinc chloride complex of (ii) has been prepared on laboratory scale. Sample has been sent to industry for testing.

Experiments are in progress to prepare the zinc chloride complex of *p*-diazo-N-di-β-hydroxyethyl-*m*-toluidine starting from N-di-β-hydroxy ethyl-*m*-toluidine. Photosensitivity of (ii) was tested by preparing test print papers incorporating (i) and (ii). The trials gave encouraging results.

38. *Theophylline-caffeine :* (ATT-77/68)

Theophylline is a useful myocardial stimulant and potent diuretic. In combination with ethylene diamine, as aminophylline, it is useful in bronchial asthma. Caffeine, which is also an important drug, can be prepared from theophylline by simple methylation.

Theophylline and its derivatives are not manufactured in the country and their imports are estimated at 30 TPA valued at about Rs. 10 lakhs.

A synthetic route starting from urea developed earlier is costly. A cheaper and efficient route starting from 1-3-dimethylurea is being investigated.

Optimum conditions for the laboratory scale synthesis have been established. Scale up work is in progress.

39. *p-tert-Butylcatechol :* (ATT-79/68)

p-tert-Butylcatechol is used as a polymerization inhibitor. At present it is entirely mported. Requirements of M/s. Synthetics & Chemicals, Bareilly, alone is estimated at 50 TPA valued at Rs. 20 lakhs. It is likely that the demand for this chemical in near future may be much higher than 50 TPA.

Starting from catechol, a laboratory scale technical preparation has been standardized. The samples were found to be superior to the imported product in purity and performance. The process developed earlier was further modified to increase the conversion and yield of the final product and to enable recovery of the catalyst and unreacted catechol for reuse. Simultaneously, the need for high vacuum fractionation of the reaction mixture was avoided by these modifications. For carrying out pilot plant scale preparation on 10 kg./batch scale, a reaction assembly has been modified and successfully used to reproduce laboratory scale results.

40. *Catechol :* (ATT-82/68)

Catechol is a relatively expensive intermediate used in the manufacture of *p*-tert-butyl catechol. It is also used in the preparation of certain drugs like adrenaline. Catechol is neither manufactured in the country, nor are the estimates for its demand or imports available.

Although the project was initially aimed at the synthesis of catechol from *o*-dicholorobenzene or *o*-chlorophenol, it has been decided to explore the possibility of isolating catechol from the polyvalent phenols which are available from the Neyveli Lignite Corporation.

The crude polyvalent phenol has been fractionated on 1 kg./batch scale and catechol has been isolated in about 12-13% yield. Catechol has also been isolated in about 33-35% from *catechol rich cut* obtained from the Neyveli Lignite Corporation.

Work is in progress to improve the yield and also for isolating methyl catechols and other components.

41. *2-Aminopyrimidine and sulphadiazine :* (ATT-81/68)

2-Aminopyrimidine on condensation with acetylsulphanyl chloride (ASC) yields the valuable sulpha drug, sulphadiazine. The high cost of this sulpha drug is mainly due to the high cost of 2-aminopyrimidine which is at present imported. Attempts are being made to synthesize this chemical from easily available cheap raw materials follwing a new route.

Attempts for direct synthesis of sulphadiazine are also in progress.

42. *Purification of anthracene :* (ATT-83/68)

Anthracene is required for the production of anthraquinone, a dyestuff intermediate. Estimated requirements of anthraquinone by 1970 are about 1300 TPA valued at Rs. 30 lakhs. Coal tar crude anthracene containing carbazol is available from steel plants.

Experiments were carried out for the enrichment of anthracene and carbazole from the crude mixture obtained from the Hindustan Steel Ltd., Bhilai.

As a result of these experiments, a laboratory scale (200 g./batch) process has been developed in two stages. In the first stage of purification, a product containing 45-50% anthracene (recovery 80%) was obtained. In the second stage, a product containing 90-95% anthracene (recovery 85-90%) was recovered. The overall recovery of anthracene of 90-95% purity was about 75%.

After removing anthracene, the residue containing carbazole was processed for obtaining pure carbazole. A laboratory scale process

(600 g./batch) has been developed yielding carbazole (95-97% purity). The recovery is 60-65%.

43. *Acetylacetone :* (ATT-84/68)

Acetylacetone is an important intermediate for the sulpha drug, sulphamethazine. The 1970-71 targetted annual requirement of acetylacetone is 320 TPA valued at around Rs. 48 lakhs. This intermediate is being manufactured by the IDPL, Hyderabad, which has scope for further improvement.

Attempts were, therefore, made to develop a new process involving a vapour phase thermal rearrangement of isopropenyl acetate over a suitable catalyst.

The preparation of isopropenyl acetate by reacting ketene and acetone was also tried. The results of these laboratory scale trials were not found encouraging and, hence, the project is abandoned.

44. *Stationary liquid phases and solid support for GLC instruments :* (AB-33/63)

With the growing tendency of using gas liquid chromatography techniques in research and industry, it is expected that the demand for column filling material (solid support) and liquid phases will be considerably increased.

Solid support : In order to test the uniformity of supports made from various types of fire-bricks available in the country and compare them with the imported supporting materials, different varieties of fire-bricks were reduced to proper mesh sizes, and their properties have been evaluated. It was observed that, in order to have the same efficiency, different treatments are necessary for different types of fire-bricks. Silanized fire-brick support shows promising results at high temperature.

Stationary phases : Polyesters containing unsaturation show unusual behaviour at different temperatures. After prolonged heat treatment further cross linking of polyester on columns is observed. They are being critically examined.

Syntheses of special polyesters for aromatic compounds have been undertaken.

45. *Conversion of dehydrocostus lactone into chamazulene and s-guaiazulene :* (AB-30/67)

This work was undertaken to find whether commercially useful azulene derivatives could be prepared in good yields from crystalline lactones obtained during the extraction of costus root oil.

Yields of azulenes by sulphur or selenium dehydrogenation of the dihydro derivative of dehydrocostus lactone were very poor. By employing alkaline dehydrogenation under different conditions, the yield of chamazulene could not be raised above 20%. The work is concluded.

46. *Phenobarbitone :* (ATT-78/68)

Phenobarbitone is a member of the group of drugs known as barbiturates. It is hypnotic, sedative and anti-convulsant and is used in the treatment of epilepsy.

M/s. IDPL, Hyderabad, are manufacturing this drug to the tune of 10 TPA. The project has been undertaken to improve the yields at various steps.

47. *Salicylaldehyde :* (AB-66/68)

Salicylaldehyde is used in the perfumery industry especially as an intermediate for the synthesis of coumarin which is being imported for its use in perfumery compositions. It has also a limited use as fungicide and larvicide. A patent claims that it is an ultraviolet stabilizer for polystyrene compositions.

Work was undertaken to study the feasibility of synthesizing salicylaldehyde by Reimer-Tiemann reaction on phenol. During the preliminary experiments, the proportion of *p*-hydroxybenzaldehyde obtained in the reaction was consistently higher than that reported in the literature. The technical preparation of salicylaldehyde by this route does not appear to be of commercial interest.

48. *Stabilized gel for hot and cold sachets :* (ATT-128/68)

On account of its large heat capacity and latent heat, water has been used extensively for applying heat or cold to the human body and for keeping food and drinks warm or cold, as desired. This use would, however, become much more convenient if a gel containing a large proportion of water could be developed which would not melt at the temperature of boiling water and which could also be frozen like ice-cream.

With this objective in view, a large number of indigenous polysaccharides were tried to prepare a stable gel of the desired consistency (water content 85-90%) with or without the aid of gelling agents. The selected stabilized gel, when filled in flexible plastic (PVC) sachets, can be heated in boiling water and used as hot water bag which stays hot longer than the conventional hot water bottle on account of the slow heat transfer through the gel. These sachets can also be frozen in a refrigerator and used in place of ice bags. These frozen sachets are colder than ice, on account of lower freezing point of the gel, and these also stay cold longer on account of slow heat transfer.

Sachets conforming to the above properties have been successfully prepared. The process is ready for release to industry.

49. *Acrylic base cation exchange resin :* (ATT-33.1/66)

These resins are mainly used in pharmaceutical and antibiotic industries. Based on the make-up requirements of the four antibiotic units in the country, the annual demand is estimated to be of the order of 10 TPA.

Work has been undertaken to prepare free-flowing, spherical resin beads of the desired volume capacity. With this object in view, laboratory scale experiments for the suspension copolymerization of methacrylic acid with divinyl benzene have been carried out under different conditions. It was possible to obtain fairly stable suspension leading to non-sticking spherical beads. However, the volume capacity was only 60% of an equivalent imported product. It has been found that the volume capacity of the resin can be regulated by varying the DVB content.

Further work on this project is temporarily suspended, as an expected bulk supply of the monomer has not been received so far.

50. *Polystyrene foams :* (ATT-34/66)

Polystyrene foams, which find exclusive use in low temperature insulation and packaging, are at present being manufactured with imported know-how. The demand in the country for polystyrene foam is estimated at 2000 TPA valued at about Rs. 2 crores.

Experiments to standardize the preparation of expandable polystyrene and low-density foam sheets have been undertaken. It has been reported earlier that the use of an indigenous suspending agent was found very effective in reducing agglomeration, and glassy, transparent beads could be obtained. By standardizing the reaction conditions, it is now possible to obtain shiny beads of required size in 70-80% yield.

Large size foamed sheets (76 cm. × 38 cm. × 10 cm.) moulded from prefoamed beads showed densities ranging from 1·1 to 1·5 lb./cft.

Work to obtain lower density sheets is in progress.

51. *Sulphochlorinated polyethylene :* (ATT-90/68)

The vulcanized sulphochlorinated polyethylene has several outstanding properties. Estimated demand of this polymer is roughly assessed at 100 TPA.

This is used for tank lining, hose and cables, coatings for ship docks, roofs, masonry, gaskets, packings, etc. If produced commercially in the country the above demand is likely to increase.

Literature survey on sulphochlorination and chlorination of polyethylene has been nearly completed. Indian patent situation on this product is being surveyed. A bench-scale reaction unit and a chlorine dispenser are under fabrication. Some auxiliary apparatus for polymer characterization has been fabricated for evaluation of polyethylene. Small scale experiments on the reaction of polyethylene and sulphuryl chloride are in progress.

52. *Nitrile rubber :* (ATT-52/67)

Nitrile rubber is a copolymer of acrylonitrile and butadiene. It is used in rubber formulations, where oil resistance is of importance, and in special adhesive formulations. Nitrile rubber is not at present manufactured in the country and is imported to the extent of 500 TPA valued at Rs. 50 lakhs.

The project has been undertaken to develop technical preparation of nitrile rubber with high, medium and low nitrile content.

As reported earlier, nitrile rubber with 34% of acrylonitrile content has been prepared in 60% yield on laboratory scale. With the introduction of a new activation system, 65 to 70% conversions have been obtained in polymerization reaction and a copolymer of 34% bound acrylonitrile produced. Short stopping the reaction and drying of the polymer have been standardized. Some of the samples prepared on laboratory scale have been sent to a firm for evaluation. The firm has reported that in processibility and physical properties, these compare well with imported material.

Scaling up experiments are in progress. Accessory assemblies for butadiene distillation, recovery of unreacted butadiene and acrylonitrile, are being fabricated.

53. *Rubberized cork sheets :* (ATT-99/66)

As reported earlier, a process for the preparation of rubberized cork sheets from cork granules has been developed and released to industry.

At the request of another firm, samples of rubberized cork sheets of different specifications have been prepared from the samples of waste cork supplied by them. The samples have been approved and further negotiations are in progress.

54. *Polysulphide rubber :* (ATT-89/67)

Polysulphide rubber is popularly known as thiokol rubber. Liquid polysulphide rubber is required for the production of rocket propellents, oil and fuel resistant sealing materials, adhesives, etc. At present, this rubber is not produced in the country and imports are estimated to be of the order of 200 TPA valued at Rs. 30 lakhs.

Attempts are being made to standardize technical preparation of this rubber.

Liquid and solid polysulphide polymers have been prepared on laboratory scale. Work is in progress to prepare solid rubber from liquid polymer by using different cross-linking agents.

55. *Utilization of coir pith :* (ATT-39/66)

This work has been undertaken to explore new outlets for the waste available in the coir industry. It may also provide a substitute for imported cork being used for the production of rubberized cork gaskets.

Rubberized coir pith sheets of different hardness (shore A 75-80 and 60) have been made and supplied to a few parties for evaluation. In response to a paper published on this subject, a Japanese firm has shown interest in this work and samples have been supplied to them.

56. *Latex foam backed coir :* (ATT-100/66)

At the instance of a private firm, work has been undertaken to prepare foam-treated coir cushions. Samples of pre-laid coir cushions have been treated with latex foam and jelling, drying and vulcanization conditions have been standardized.

Cushion samples, so prepared, have been sent to the interested party for evaluation.

57. *Rubber reclaiming agents :* (ATT-51/66)

With the use of rubber reclaiming agents, vulcanized scrap rubber can be regenerated to its orignal plastic state permitting the product to be processed, compounded and revulcanized. Rubber, reclaimed by this process, is used in the preparation of tyres, tread rubber, automobile floor mats, battery containers, soles, heels, etc. The production of reclaimed rubber in India is estimated to be about 11,000 tonnes. By 1971, the production is expected to be over 25,000 tonnes. Accordingly, the demand for the reclaiming agents in 1971, can be estimated to be about 250 tonnes valued at approx. Rs. 25 lakhs.

Different types of reclaiming agents are used for different reclamation methods. Work has been undertaken to develop technical preparation of one such reclaiming agent based on totally indigenous raw materials. The preparation based on xylene and sulphur monochloride has been standardized on pilot plant scale. The product has been approved by the industry and the process has been released to a party, who has already started large scale production of the reclaiming agent.

58. *Rubber blowing agents:* (ATT-117/63)

Blowing agents are used in the production of microcellular expanded rubber articles. Dinitrosopentamethylene tetramine (DNPT) is one such blowing agent which has already been made by a few firms in the country. The total demand of the country is estimated at about 150 tonnes per year, valued at Rs. 15 lakhs. DNPT, if not properly stabilized, explodes or catches fire in the mixing mill. Since the indigenous product is often not properly stabilized, work on the technical preparation has been standardized on 10 kg./batch scale and the samples have been evaluated. The process has been released to a party, which has started production.

59. *Styrenated alkyds:* (ATT-97/67)

Styrenated alkyds are known to be superior to ordinary alkyds in their various applications in paint technology. Preparation of the resin has been successfully carried out in the laboratory upto 10 litre/batch scale. By making a few changes in the method of styrenation and polymerization, the reaction time has been reduced and a product having good film forming properties and notable pot life has been obtained. Representative samples of the resin have been sent to a few paint manufacturers in the country for evaluation. The work on this project is concluded.

60. *Linseed oil emulsions:* (ATT-49/66)

The project is aimed at the development of a low cost water thinnable linseed oil based emulsion for use in place of plastic emulsion paints.

As already reported, linseed oil, polymerized in the presence of SO_2 and CO_2, has given better emulsions than the vacuum heated polymerized oil. A pale yellow product has been obtained when refined linseed oil is used, but with raw linseed oil a dark coloured product has been obtained. Uniform emulsions have been prepared using a vertical colloid mill. Incorporating wet ground titanium dioxide and talc, thickening agent and drier, a blue tinted emulsion paint has been prepared and used for painting two rooms ni the laboratory. The performance has been found comparable to commercial plastic emulsion paint but has a less smooth finish. Emulsion paints, so obtained, when applied on external masonry surfaces have not undergone any changes due to seasonal variations. Samples have been sent to a few firms for evaluation.

61. *Coating for nylon fabric:* (ATT-47/64)

At the initiation of SASMIRA., Bombay, shellac, castor oil and TDI (toluene di-isocyanate) based coating formulations have been prepared and used for coating nylon fabric. Nylons coated with this type of composition are used for making high altitude hutments etc. Fabrics, thus, coated have been tested and found to agree with specifications needed by Defence. Samples have been sent to Defence Laboratory, Kanpur, and SASMIRA., for evaluation. Since their reports are encouraging, the process is being offered to industry.

62. *Leather coatings:* (ATT-103/68)

At the initiation of a football manufacturer, a castor oil-isocyanate based coating composition has been prepared on laboratory scale and tested, particularly, for water repellency, gloss and flexibility. The coated samples have been evaluated by actual field trials and found satisfactory. These coatings can also be used in rubber and foot-wear industry. The work is successfully concluded and the process is available for release.

63. *Resins for automobile filters:* (ATT-116/63)

At the initiation of a local filter paper manufacturer, a coating composition based on phenol-formaldehyde resin, suitable for applying on filter papers and helpful in filtering automobile oils free of water, has been developed. Samples of filter papers coated with the composition has been found satisfactory in actual trials. The process has been released and the party has undertaken experimental production.

64. *Isocyanate-based coatings:* (ATT-41/65)

Starting from anacardol (from CNSL), polyamines have been prepared on laboratory scale. Polyisocyanates have been prepared by phosgenating these amines.

Coating compositions prepared from the polyisocyanates have been evaluated by SASMIRA. Bombay, and M/s. Monsanto Co., U.S.A., who have recommended that these could be used for making shower proof fabrics. Since reports from both the above parties are encouraging, large scale preparation of polyisocyanate and its coating on fabrics will be undertaken.

65. *Diamond setting cement :* (ATT-40·3/66)

A special type of imported cement is, at present, used in Indian diamond industry for setting diamonds for polishing. Study of chemical composition of the resin used in the imported cement has revealed that the resin is a linear mixed polyester of terephthalic acid.

Experiments have therefore been undertaken to develop technical preparation of the resin. Conditions for the preparation of the required resin with desired softening point and hardness have been established. Samples have been prepared under different experimental conditions and sent to different diamond cutting firms for actual trials. Although reports from many of the above firms are encouraging, the flexibility of the resin and the strength of the cement needs certain improvements. Further experimental work has been undertaken to standardize the preparation of the cement.

66. *Rubber base adhesives :* (ATT-42/66)

Work on adhesives needed by the HAL, Bangalore, is being continued. A few more samples of the type Bostik-1752 and Bostik-1753 have been prepared and tested in the laboratory. These samples have been further tested on the HAL site in presence of the NCL scientist. Both the tests have been found concurrent and satisfactory, particularly, towards fuel resistance. Subsequently two more samples have been sent and found satisfactory in all respects. Samples similar to Bostik-1790 have been prepared and sent for evaluation to the HAL, Bangalore.

67. *Materials for artificial limbs :* (ATT-88/67)

Artificial Limb Centre, Poona, are making use of a synthetic foam material for making artificial limbs. Imported samples of this material have been analysed and found to be a polyol mixture of which the main constituent is a polyether of low viscosity. Since these types of polyethers are not locally available, a mixture of locally available polyether and NCL made polyester has been used for making a polyol of the correct hydroxyl number. Foams prepared from this polyol and TDI have properties similar to the imported foam materrial used for making artificial limbs. These foams have been made only in small sizes. Larger size foams will be prepared for evaluation in the Artificial Limb Centre, Poona.

68. *Composite propellents :* (ATT-37/63)

A castor oil based formulation for making composite propellents has been developed and sent to Space Science Technology Centre, Thumba, (SSTC), for evaluation. In this connection, NCL scientist visited SSTC and the technique of making composite propellents was demonstrated. Rocket motors have been fire tested and found suitable. A vacuum mixing casting machine is being fabricated for SSTC. The polymers supplied by the NCL have been found acceptable in their experimental trials.

69. *Sealants for canvas bags :* (ATT-129/68)

At the instance of the Defence department, work has been undertaken to develop a sealing composition capable of making polythene-lined canvas bags leak proof. The bags used, at present, leak through the stitches and during transportation stitches get open.

The developed composition has firmly held the stich ends and except for the pot life, the NCL composition has been found suitable for the above purpose. In order to improve upon the pot life, new compositions have been made, of which a representative sample is found to remain workable for more than 6 months.

70. *Synthetic polymers for oil well drillings:* (ATT-115/68)

Oil and Natural Gas Commission, New Delhi, (ONGC), has approached the laboratory to develop a substitute for an imported cement additive (Halad) used in oil-wells. This water soluble polymer when added about 1% by weight to cement, prevents quick water losses from the cement slurry and hence, helps in proper setting of the cement. At present, the import of this product is estimated to be worth about Rs. 4 lakhs /year.

Preliminary investigations have been undertaken to examine the imported product. Derivative of polyvinyl alcohol has been tried as a possible substitute but found to be not effective in preventing water losses from the cement. Analysis of 'Halad' indicates that it is a mixture of a carbohydrate derivative and sulphur containing substances.

71. *Synthetic polymer for cane juice clarification :* (ATT-86/68)

Indian sugar mills have been, hitherto, using an imported product sold under the trade name 'Separan AP-30', for the clarification of cane juice. The demand for this product is estimated to be worth Rs. 10 lakhs per year.

Preliminary analysis suggests that Separan is a water soluble polymer based on acrylamide. The systematic study of the polymerization of acrylamide in aqueous solution has been carried out to obtain a polymer of the desired properties and molecular weight. The polyacrylamide, thus, obtained is hydrolysed so that 30% of the acrylamide units are converted to acrylic acid. Samples of the products, so prepared, have been sent to three sugar factories for evaluation. Two of the samples are reported to be comparable to the imported product. Large quantities (5-10 kgs.) of these samples have been requested by the factories for large scale trials.

72. *Utilization of a bye-product available in the manufacture of terephthalic acid :* (ATT-114/68)

At the request of ONGC, New Delhi, studies have been undertaken to explore the possibilities of using a mixture of dimethyl terephthalate and dimethyl isophthalate (a bye-product obtained in the manufacture of terephthalic acid) in the preparation of polyester resins for surface coatings. After establishing the conditions of reaction, alkyd resins with different compositions have been made and their film forming properties and other characteristics determined. Based on these results, a report has been sent to ONGC, for further action.

73. *Micro filters :* (ATT-87/68)

These filters are employed in a variety of filtration jobs in dyes, pharmaceuticals, foodstuffs and other industries.

Exploratory experiments for preparing filter cartridges using cotton linters, wood cellulose, wool, jute, together with phenol formaldehyde and melamine-formaldehyde resins have been carried out. Samples prepared are being tested.

74. *Xylene formaldehyde resins :* (AB-53/67)

These resins are used as plasticizers in paints. They could also be made into thermosetting resins. At the initiation of a private party, preliminary experiments have been made and samples supplied. The firm has suggested some modifications to be made in the resin and attempts are being made to modify the same in the light of these suggestions.

75. *Foundry chemicals :* (ATT-54/66)

During the last few years Indian foundry industry has made rapid progress in quality mouldings of variety of engineering goods and in total tonnage moulded. Although, some of the foundry chemicals are at present, manufactured in the country, it is imperative to develop right type of foundry chemicals which play an important part in cost and quality of the finished goods.

75·1 *Shell moulding resin :* (ATT-54·1/66)—Shell moulding process is important for casting sophisticated engineering goods with high dimensional accuracy and finish. Usually phenol-formaldehyde resins are used in shell moulding compositions. Since phenol is not yet made in the country, attempts have been made to use indigenously available phenolic raw materials for the purpose.

Compositions based on CNSL-formaldehyde lignin condensates have been prepared and tested for their curing, baking and mould release properties. A composition found suitable in the laboratory has been sent to industry for evaluation. On the basis of the test report, further work will be undertaken.

75·2. *Sinol core binder :* (ATT-54·2/63)—This type of core binder is used in steel foundry, wherein sand cores possessing high tensile strength and giving minimum of smoke are required.

Compositions developed earlier have been made using an imported material as a catalyst. In order to avoid the use of imported catalyst and to minimise production cost, development of new compositions have been undertaken. Samples have been made using different indigenous materials as catalyst and the one found satisfactory in laboratory trials has been sent to industry for performance trials. On the basis of the evaluation report, further work will be undertaken.

75·3. *Dry core binder :* (ATT-54·3/65)—This binder is based on dextrinized starch and certain inorganic materials.

Compositions based on calcium salt of lignosulphonic acid isolated from Indian magnesium based sulphite liquor and certain agricultural waste, have been prepared and tested in the laboratory. A sample, which gave promising result, is being made in larger batches and will be sent to industry for evaluation.

75·4. *Starch phosphate :* (ATT-54·4/64)—This product finds use in the food and adhesive industry, ore refining and foundry work. Preliminary trials have shown that it gives good green strength and contributes to dry and hot strength in sand cores and requires no addition of oil for ordinary castings. In speciality castings with the use of this product only half of the quantity of oil is needed. In order to evaluate the product as an additive to food preparations, samples have been sent to a few food manufacturers, CFTRI, Mysore, and Food Department of Chemical Technology, Bombay. The product is also being evaluated as slime depressant in ore refining.

75·5. *Double boiled linseed oil substitute :* (ATT-54·5/67)—A composition which works as a cheap substitute for double boiled linseed oil (used as traditional sand binder in foundries) has been produced on 250 kg./ batch. Dextrin which is commonly used as an adjunct to core oil to impart necessary green strength to sand cores has been incorporated in this composition. However, the composition has been found non-compatible with tamarind kernel powder (TKP) used as dextrin substitute.

Work has been undertaken to modify the composition suitably so that TKP may be incorporated. A sample, which was found suitable in the laboratory, has been sent to industry for evaluation.

76. *Low temperature fluxes :* (ATT-85/67)

These are used for soldering electrical contacts in electronic circuits and are at present imported. One of the components of these fluxes is known to be glutamic acid, which is not produced in India at present. Attempts have therefore been made to prepare low temperature fluxes based on entirely indigenous raw materials. One sample which showed promising results is prepared on laboratory scale and has been sent to industry for evaluation.

77. *Substitute for dextrin :* (ATT-130/68)

Tamarind kernel powder is a bye-product of the tamarind pulp industry. It is estimated that about 90,000 TPA of tamarind seed kernel is available in the country. It is reported that over 30,000 TPA of tamarind seed kernel is marketted in the country for its use in various industries. It is also used in Indian foundry industry as a substitute for dextrin.

Phosphorylation of tamarind kernel powder has been attempted and promising results have been obtained.

78. *Chlorobenzenes :* (ATT-118/68)

Monochlorobenzene (MCB) is used in the manufacture of dye intermediates, nitrochlorobenzene, DDT and phenol. *o*-Dichlorobenzene (ODCB) is used as a solvent to remove deposits from engine parts, as a heat transfer medium, coolant for magnetic coils, rust-proofing agent, degreasing agent, etc. *p*-Dichlorobenzene (PDCB) is mainly used in the production of moth repellents and air deodorant compositions.

The investigation on the development of a process for the manufacture of chlorobenzenes has been undertaken at the instance of Hindustan Organic Chemicals Ltd., Rasayani, (HOC), which required a plant to produce 3,500 tonnes of monochlorobenzene (MCB) and 900 tonnes of dichlorobenzenes (PDCB & ODCB) per year. The developmental work on a pilot plant scale has been started in April, 1968.

In the chlorination of benzene, it is not possible to get exclusively MCB (b.p. 132°), and the product contains the two isomeric dichlorobenzenes, PDCB (m.p. 53°, b.p. 174°) and ODCB (b.p. 180·3°) in proportions depending on the chlorinating conditions. The process developed by NCL involves continuous contacting of chlorine and dry liquid benzene in a recirculating type tower reactor, packed with Raschig rings and provided with facilities for the extraction of exothermic heat and temperature control. The drying of benzene is achieved by sodium hydroxide followed by contacting it with hydrogen chloride generated in the reaction. The crude product from the reactor is treated with lime and is fractionated in distillation columns to get benzene, MCB and DCB. Subsequent separation of DCB isomers is done by crystallization.

The complete developmental work has been done in a pilot plant of about 200 kg. per day capacity. The reaction condition, as optimized in this plant, gives a consistent overall conversion of benzene of about 70% which is considerably higher than the conversions reported by several other processes in which also MCB is the predominant product. Based on the process and engineering data collected, a larger pilot plant of about one tonne per day capacity has been designed. This plant has been erected by a project engineering firm in Bombay, at their factory. The operation and standardization of this plant have also been successfully carried out.

The process design for a plant of 4,400 tonnes per year capacity (as required by HOC) has also been completed.

79. *Ethylenediamine :* (ATT-58/66)

Ethylenediamine is an important starting material for the manufacture of many industrial organic chemicals and is used in the manufacture of organic fungicides, pesticides, rubber chemicals etc. At present, the chemical is not produced in the country and the total projected demand for 1970-71 is estimated to be around 1200 TPA valued at Rs. 90 lakhs. As already reported, a process for producing ethylenediamine from ethylenedichloride and ammonia has been standardized by statistical methods.

Using this data, a continuous pilot plant of about 5 kg./ hour has been designed and erected. The necessary engineering design data will be collected during the operation of this plant.

80. *Chlorination of methane gas :* (ATT-92/67)

In collaboration with a project engineering firm in Bombay, 2·5 kg./hr., capacity carbon tetrachloride and chloroform plant has been operated at

Sewage Purification Works, Dadar, using raw sewage gas containing about 60% methane.

It is proposed to utilize the methane gas available from the naphtha-craker in a petrochemical complex at Bombay for chlorination. The methane gas could be piped to an adjoining caustic-chlorine works where abundant chlorine is available. The costing of such an integrated plant, on a semi-commercial basis, has been entrusted to a project engineering firm in Bombay.

Preliminary assessment of the cost requirements will be forwarded to the firm for a plant of 300 tonnes capacity of carbon tetrachloride and chloroform per year.

81. *Ethyl acetoacetate :* (ATT-94/68)

Experimental work on the recovery of ethyl acetate from the 20-80% (by weight) ethanol-ethyl acetate binary by liquid-liquid extraction with aqueous potassium acetate solution has been continued. Cross-current-multiple-contact procedure has been followed using fresh solvent for each stage. It has been found that it would be possible to separate about 90% of the ethyl acetate originally present in the binary by this technique and that the purity of the ethyl acetate thus recovered would be about 98%.

82. *Preparation of sorbitol and mannitol from invert sugar :* (ATT-55/66)

A method to estimate sorbitol and mannitol in a mixture of polyols has been developed. The total mixture has been first acetylated and the acetates separated by VPC.

The earlier hydrogenated product, when tested by this method, has shown the presence of a third unidentified component in fair proportion. Conditions of hydrogenation have therefore been modified and it has been possible to reduce this component to small proportions and get the desired products in about 95% yield.

When the catalyst was reused, it gave colourless product and the reaction was over in the optimum time for three runs. During further runs, there was some development of colour and the time of reaction also increased.

Separation of the mannitol as a crystalline product has been studied using synthetic mixtures of the two polyols in the proportion expected in the hydrogenation.

A tentative method giving yields of over 85%, based on the mannitol present, has been worked out. The mannitol appears to be pure from its melting point and will be checked by VPC analysis. Further work to improve the recovery of mannitol and, simultaneously, the purity of residual sorbitol syrup will be carried out. The method so developed will be finally tried on the actual hydrogenated mixture.

Further work to improve the process in all its aspects will be continued.

83. *Phenacetin :* (ATT-91/67)

Phenacetin is used as an analgesic and antipyretic agent in the pharmaceutical industry. Although a few firms are manufacturing phenacetin in the country, present imports are about 210 TPA valued at Rs. 23 lakhs.

The acetylation of *p*-phenetidine has been carried out in high yields by an improved process, wherein the time cycle has been reduced to only 5 hours. Large scale trials of 100 kg./batch, for the preparation of phenacetin from *p*-phenetidine have been carried out.

84. *Analytical vapour phase chromatograph :* (ATT-63/67)

The vapour phase chromatograph is finding increasing applications as a versatile and powerful analytical tool in both the chemical research and industry. These units are presently imported and the prices vary from Rs. 25,000–50,000 per unit.

A vapour phase chromatograph consisting of dual injectors, an air circulating column oven, a detector cell oven with variable heat control, dual columns, dual detector cell and dual collectors, has been developed. The design and the fabrication know-how has been released to a firm on exclusive basis and the party has already produced some units based on the NCL know-how.

85. *Preparative vapour phase chromatograph :* (ATT-123/69)

Preparative vapour phase chromatograph (VPC) is becoming an indispensable instrument in a modern research laboratory.

Considerable work has been carried out for developing the instrument for preparative VPC. Preparative column was made and tested for resolutions with 0·05 ml. of sample injected; good resolutions were obtained. Accordingly, modifications were carried out in the injector heating system and thermal capacity detector.

Work on automatic collector and injection systems is in progress.

86. *ESR spectrometer :* (ATT-61/68)

ESR spectrometers are being used for analytical work and for research. These instruments are at present imported (cost Rs 2-3 lakhs). The equipment to be developed will be useful for research work as well as for teaching in universities.

The circuits of the ESR spectrometer system, which has been under construction have now been transistorized wherever possible and these new circuits are being tested. All these circuits are being incorporated in the newly constructed console. Some units are rebuilt to get better performance. Klystron power supply is refined from this point.

Flat bed recorder servo amplifier is tested and mechanical assembly is under way. Magnet cabin is constructed and the allied circuits—pre-amplifier phase sensitive detector are placed in position. Magnet power supply is nearly in the finished stage of assembly.

87. *Self-balancing strip-chart recorder :* (ATT-63/67)

Potentiometric recorders of the type developed in NCL are not manufactured in the country and the entire requirement is met by imports. It is a very versatile instrument and is capable of being used for a variety purposes i.e. with instruments such as vapour phase chromatograph and NMR, EPR, IR and UV spectrometers, polarigraphs, etc. In addition it can also be used along with many industrial process control devices.

Developmental work on the designing of the above type recorder was completed and a unit was fabricated with following specifications:

Electrical:

Span (full scale voltage):	1 mv to 50 mv adjustable in 5 ranges
Response time:	2·5 seconds (min.)
Input resistance:	50,000 ohms
Zero suppression:	One full scale
Sensitivity:	0·25%
Accuracy:	0·5%
Power requirements:	230 volts, A.C. 50 c/s 30 watts

Mechanical:

Dimensions:	Height–10·5″ Breadth–13·00″ Width–18·5″
Weight:	18 kg.
Chart width:	10″
Chart speed:	Normally 15″ per hour. Can be changed with gears to lower and higher speeds. Any special speed can be incorporated.

Extensive performance tests were conducted with a gas chromatograph and the results were found quite satisfactory. Negotiations for the release of the fabrication know-how are in progress and a prototype has been fabricated for consumer's evaluation.

88. *Fabrication of a precision ultrasonic interferometer* : (ATT-124/69)

Measurement of ultrasonic velocity provides very valuable information about liquid state properties such as adiabatic compressibility, specific heat at constant volume (C_V) which *inter alia* are used for elucidating the nature of molecular interaction.

Basic work on the development of an ultrasonic interferometer has been carried out and a complete unit has been designed and fabricated. The instrument is being used at present for compressibility measurements of some polyelectrolytes. This type of instrument is not as such available in the market, however, it is felt that many universities and research institutions where physical properties of liquids are studied may need such an instrument.

The design of the instrument is being further modified so that the prototype and the fabrication know-how can be released to interested parties.

During the period under report some modifications of the present unit have been undertaken so that nodal positions can be conveniently observed on a built-in cathode ray oscilloscope. All individual parts for the same have been fabricated and tested in part-wise manner. These are being assembled and tested in the old unit.

89. *Equipment for the determination of total solid content in latex compositions, cements and adhesives* : (ATT-53/67)

The equipment is meant for the quick determination (in 6-8 minutes) of the total solid content in a latex composition. Steps have been taken to fabricate a few more testing units which on assembly will be sent to outside parties for evaluation. The original unit prepared in the laboratory is in use.

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RESEARCH PROJECTS

1. THEORETICAL INVESTIGATIONS IN SOLID STATE

1·1 *The ligandfield theory of trigonal bipyramidal complexes:* (B-1·9/68)

The treatment is of the strong field type making no simplifying assumptions beyond those demanded by the symmetry of the molecule.

The five-fold manifold corresponding to a single *d* electron of a free ion gets resolved under D_{3h} symmetry into a'_1 spanned by d_{z^2}, e' spanned by d_{xy} and $d_{x^2-y^2}$, and e'' spanned by d_{yz} and d_{xz}. Thus there are three levels and two crystal field parameters, Δ_1 and Δ_2. With two *d* electrons there are six possible strong field configurations and the corresponding product representations decompose into 17 terms in all. The corresponding Clebsch-Gordan coefficients and hence the basis functions were worked out. The matrix elements of inter-electronic repulsion which are diagonal only for non-repeating terms were then calculated by treating the crystal field orbitals as equivalent to those of the free ion, and in terms of the Racah parameters A, B and C. The orbital energies in terms of Δ_1 and Δ_2 were then added to the diagonal elements, and the resulting secular determinants were then solved on the IBM- 1620 computer for a series of values of

$$\Delta_1/B \ (0 \leqslant \Delta_1/B \leqslant 8) \text{ and } \Delta_2/B \ (0 \leqslant \Delta_2/B \leqslant 35)$$
$$\text{where } \Delta_1 = E_{e'} - E_{e''}, \text{ and } \Delta_2 = E_{a'_1} - E_{e''}$$

The energy level diagrams were then drawn one for each term as a series of constant energy contours with Δ_1/B and Δ_2/B, plotted along the two coordinate axes. These energy level diagrams which allow for the mutal independence of the two parameters are also applicable to symmetries, C_{3v}, D_6, D_{6h} and C_{6v} with trivial modifications. Allowing for the nephelauxetic effect, these curves are very handy for the interpretation of the ligand field spectra of such complexes.

The calculations have been completed for the nickel ion. They are now being extended to the case of the vanadyl ion.

2. MATERIALS FOR SOLID STATE DEVICES

2·1 *Ferroelectric materials:* (AB-2/57)

In recent years ferroelectric ceramics are commercially used in phonograph pickups, ultrasonic transducers for high power generation, ceramic wave filters and memory and display devices. Our investigation is aimed at preparation of ferroelectric ceramics of a new and improved type, and a detailed sudy of their structural, dielectric and other properties in relation to their ferroelectric and associated piezoelectric properties.

Doped lead titanate ceramics of the general formula $Pb\left[La_{0\cdot5}\left(B_{II}{}^{5+}\right)_{0\cdot5}\right]_x Ti_{1-x}\,O_3$ where $B_{II} = Nb$ or V were prepared and their properties studied. The results have been published.

For using the ferroelectric ceramics for phonograph · pickups these should have high dielectric constant and electromechanical coupling coefficient. To improve these properties in that direction, doping with other materials such as WO_3, MnO_2, SrO, etc., are being tried. By substituting 5% of lead with Sr, spontaneous polarization of the material can be increased to 14 Micro Coulb./cm^2.

2·2 *Chalcogenide spinel semiconductors :* (B-1·10/68)

A study on the structural, electrical and magnetic properties of $A(Cr_2\,O_4\text{-}ACr_2X_4)$ systems, where A is divalent transition metal ion, and X is S, Se or Te has been initiated. The compounds $A(Cr_2X_4)$ show interesting magnetic properties and change between para, ferro, ferri and antiferro status on small variations in chemical composition. The solid solutions formed with oxide spinels is therefore expected to show a range of magnetic properties and light on the magnetic interactions in these solids.

Doped samples of Cd Cr_2Se_4 (p and n type) have been prepared and their electrical properties studied.

Attempts are being made to develop p-n junctions in this material.

A new chemical method of preparing thin films of cadmium chromium chalcogenide is being attempted.

2·3 *Metal-insulator-metal sandwiches :* (B-2·3/64)

Studies on metal-insulator-metal sandwiches have assumed great importance in view of the recent developments in thin film devices. Earlier, interesting bistable conductivity switching and memory phenomena in some Al-CdSe/Te-Au sandwiches was observed. The mechanism of these phenomena have been studied in detail with the help of experimental data on steady state and dynamic current-voltage-temperature dependence, photo-conductivity, photo-voltage, relaxation effect, pulse measurements, etc. It has been established that the Au-CdSe and Au-CdTe contact is ohmic and Al-CdSe and Al-CdTe contact is blocking in the samples. At Al-CdSe/Te interface, the barrier is created due to the combined action of the surface state and surface barrier layer. The oxygen ions taken up at the interface play an important role in the creation of the surface barrier layer. The two conductivity states have been attributed to the presence or absence of the barrier at Al-CdSe/Te contact. The barrier can be reversibly created or destroyed by the application of electric field of appropriate polarity. This property of the barrier leads to bistable conductivity and switching in the samples.

2·4 *Photoconducting materials :* (AB-5/62)

During the period under review, work was carried out on the following topics:

The spectral response of photoconductivity of chemically deposited layers was studied at temperatures 313° - 73°K. A shift in the peak response with temperature has been recorded. Both pure and doped samples were studied and the shift in spectral response peak is attributed to the presence of donors with a lower energy than that for the intrinsic CdS material. The spectral absorption curves were recorded in the wave length region 300 to 700mμ. The absorption edge obtained from this measurement agrees with expected values based on a comparison with single crystals.

The dark and photoconductivity behaviour was studied as a function of temperature in the region 313° - 73°K. Activation energy values obtained from a plot of log conductivity *versus* 1/T gave values between 0·09 and 1·3 eV. These values are in close agreement with those for CdS crystals. Slow photocurrent relaxations and an interesting 'Storage' effect were recorded. The relaxations of photocurrent were observed at various intensities and at temperature 313° - 73°K. Trapping effects are believed to be the cause of the 'Storage' effect.

2·5 *Magnetic properties of decomposition products of iron oxalates :* (AB-45/68)

The study of saturation magnetization of the iron oxides obtained by the decomposition of ferrous oxalate under different gas atmospheres showed that the reddish brown product obtained in the presence of oxygen is non-magnetic alpha ferric oxide. In the absence of oxygen, the product is black and highly magnetic. Its colour and saturation magnetization 92-106 gauss cm^3/g. are close to the properties of Fe_3O_4, but its composition when studied thermogravimetrically, was found to be closer to that of Fe_2O_3 than Fe_3O_4. It is possible that Fe_3O_4 first formed, may be in such a highly divided and active form that it may pick up oxygen from the atmosphere. X-ray studies also showed the structure to be close to that of gamma ferric oxide. This black oxide was found to turn into brownish red stable gamma iron oxide at and below 250°.

The saturation magnetization of this gamma iron oxide was found to be 70-76 gauss cm^3/g. Its coercivity was found to be 260 oersteds and its remanance 1700 gauss. These magnetic properties compare favourably with those of a commercial imported sample of magnetic iron oxide.

Further improvements in these magnetic properties by varying the conditions of preparation of ferrous oxalate are under investigation.

3. NUCLEAR AND RADIATION CHEMISTRY

3·1 *Studies on Mössbauer effect:* (B-3·1 and 3·2/67)

The MÖssabauer spectra of inverse oxidic spinels containing Sn^{4+} ion viz., (i) $SnCo_2O_4$ (ii) $SnMg_2O_4$ (iii) $SnZn_2O_4$ and (iv) $SnMn_2O_4$ were studied. The compounds were prepared by solid-solid reactions at high temperature and their crystallographic 'a' parameters were found to be 8·61 Å, 8·57 Å, 8·59 Å and 8·77 Å respectively. The MÖssbauer spectra of all these spinels had isomeric shifts in the range of 0·1-0·3 mm./sec., characteristic of high spin stannic compounds and had a symmetric doublet which may be interpreted as a quadrupole splitting due to a net electric field gradient at the octahedral site due to two opposing trigonal fields, one arising due to the departure of the six nearest oxygen neighbours from ideal octahedral symmetry and the second due to the asymmetric charge distribution of the next nearest cation and anion neighbours of the octahedral site.

The MÖssbauer spectra of Fe (II) (1-10 phenanthroline)$_3$ $(ClO_4)_2$, Fe (III) (1-10 phenanthroline)$_3$ $(ClO_4)_3 \cdot H_2O$ and Co(III) (1-10 phenanthroline)$_3$ $\cdot 2H_2O$ were obtained at —194°. The values of the isomer shift relative to 310—stainless steel and the quadrupole splitting for Fe(III) (1-10 phenanthroline)$_3$ $(ClO_4)_3 \cdot H_2O$ former were 0·26 ± 0·04 mm./sec. and 1·64 ± 0·04 mm./sec. respectively. For Fe (II) (1-10 phenanthroline)$_3$ $(ClO_4)_2$, both the above MÖssbauer parameters had the value 0·40 ± 0·04 mm./sec. The MÖssbauer spectrum of Co(III) (1-10 phenanthroline)$_3$ $(ClO_4)_3 \cdot 2H_2O$ was found to be complex and analysed to be a combination of a MÖssbauer spectrum of low spin Fe (III), with isomer shift relative to stainless steel and quadruple splitting of 0·22 ± 0·04 mm./sec. and 1·72 ± 0·04 mm./sec. respectively, and a MÖssbauer spectrum of high spin Fe^{2+} with an isomer shift of 1·22 mm./sec. relative to stainless steel and a quadrupole splitting of 1·00 ± 0·04 mm./sec. respectively. The observation of the unexpected high spin Fe^{2+} state is taken to be an evidence for the fragmentation of the metal-complex due to coulombic repulsion arising out of the secondary

Auger process following the electron capture decay of 57 Co in the metal complex

3·2 *Hydroxylation of aromatic hydrocarbons by radiolysis:* (B-3·3/67)

3·2·1 *Thermal hydroxylation of benzene alcohol :* A mixture of benzene (94·5 mole %) and alcohol in presence of air, yields at 300° an optimum 1·5% conversion to phenol in one hour. The effects of temperature and the role of oxygen were also studied. At 250° the yield is nil, at 350° it is 1·8% and at 400° it levels off at 1·9%. Contrary to expectation, the replacement of air with oxygen did not lead to explosive reaction but did raise the optimum yield to ~4·5% in a mixture ~80 mole % of benzene. The reaction time is half an hour. The role of oxygen seems to remove hydrogen atoms from the intermediate radical responsible for phenol formation.

3·2·2 *γ-Radiolysis of the aqueous benzene system :* In addition to phenol ($G = 1·7$) a second compound ($G = 1·2 - 1·3$) is produced when OH radicals attack benzene in this system. I.R. and U.V. and molecular weight studies led to its identification as β-hydroxy mucondialdehyde. Methods of analysis of the compound based upon its reaction with *p*-nitrobenzene diazonium chloride, and its absorption maximum at 345 mμ have been standardized. The extinction coefficient is 4085 at 345 mμ.

3·2·3 *Catalytic effect of Fe^{2+} ions :* In the detailed study of this phenomenon (reported by Proskurnin) the Dewhurst chain mechanism was found to be completely valid. The Fe^{2+} ion at 10^{-3} M raises the yields of phenol and β-hydroxymucondialdeyde, in an identical fashion by a factor of 5·2 (G phenol = 8·8; β-hydroxymucondialdehyde = 6·5). The sum of these two compounds in this system always gives G(OH).

3·2·4 *Radiolytic amination of naphthalene :* At room temperature, γ-radiolysis of mixtures of naphthalene with a series of ammonium salts yielded no detectable quantities of naphthylamine. Radiolysis of NH_3 and naphthalene vapour mixtures also did not yield any measurable quantity of the amine below 250°.

3·3 *Diffusion of rare earth metals in copper :* (B-2.1/67)

In continuation of the previously reported work on the diffusion of ^{147}Pm, ^{160}Tb, ^{170}Tm and ^{177}Lu in copper, the diffusion of ^{141}Ce and $^{152+154}$Eu in copper was also carried out in the temperature range of 700°-980° by the residual activity method as well as by the sectioning method. The diffusion coefficients of these rare earth metals determined from the volume diffusion profile was found to vary linearly with the reciprocal of the absolute temperature and hence, can be expressed as follows :

$$D_{Ce/Cu} = 3{\cdot}01 \times 10^{\;8} \exp\left(- \frac{27943}{RT} \right) \text{cm}^2/\text{sec.}$$

$$D_{Eu/Cu} = 1{\cdot}14 \times 10^{-7} \exp\left(- \frac{26651}{RT} \right) \text{cm}^2/\text{sec.}$$

The diffusion profile when analysed by the sectioning technique showed that the plot of log specific activity *versus* square of the penetration distance was in the form of a curve, which was analysed to consist of two straight lines of different slopes. The diffusivities calculated from the slope of the first straight line (which extended to < 20 mμ) were in good agreement with those obtained by the residual activity method for the same annealing temperature. At a fixed temperature, the value of D calculated from the slope of the second straight line was found to vary from specimen to specimen indicating that the second diffusion profile was structure sensitive. The first straight line portion was attributed to the volume diffusion and the second straight line portion to the diffusion through the crystal imperfections. The low value of D_o and hence D has been attributed to the low concentration of vacancies in the region < 20 μm under the free surface of the diffusion specimen.

The values of the activation energy for the diffusion of the rare earth tracers ^{141}Ce, $^{152+154}$Eu, ^{147}Pm, ^{160}Tb, ^{170}Tm and ^{177}Lu in copper calculated from the elastic model of Swalin have been compared with the values obtained experimentally. It may be observed from the table that there is a fairly good agreement between the calculated and the experimental values of Q except for the impurity diffusion of Tm in Cu.

Solute	Q Kcal/mole (Exp.)	Q Kcal/mole (Cal.)
Ce	27·94	29·36
Eu	26·65	28·96
Tb	26·06	30·52
Tm	23·25	29·08
Lu	28·15	29·04

4. THERMODYNAMIC STUDIES

4·1 *Thermodynamic properties of solutions :* (B-13·2/63)

Ultrasonics provide a powerful tool for studying the characteristics of solutions and give valuable information concerning the coulombic interaction of ions and their dissociation mechanism. Since polyelectrolyte solutions possess both electrolytic as well as chain molecular properties, compressibility measurements in these solutions are expected to give interesting results.

The results of adiabatic compressibility of polymethacrylic acid and its sodium salts have been published. The work has been extended to other structurally similar polymers such as polymethacrylamide. The values of apparent molal volume, ϕV_2 and apparent molal compressibility, ϕK_2 at infinite dilution showed a marked change between monomer and polymer. The decrease of 19·5 cc/mole and $7 \cdot 4 \times 10^{-4}$ cc/bar/mole for ϕV_2° and ϕK_2° values respectively in polyamide over the monomer values were due to its assumption of chain-like structure on polymerization. Unlike the polyacid, the polyamide was free from the effect of the charged groups on the chain as well as from the effect of free counter ions in solution and hence, no noticeable changes were observed in compressibility data in dilute region. Since in polyacid, the compressibility was found to have been influenced appreciably due to solvation of counter ions and their concentration in dilute solution, the study of some other polyelectrolytes such as poly (vinyl N-n butyl pyridinium bromide) where counter ions are not solvated on dissociation in dilute region is expected to give somewhat different result. The work has been extended to this polyelectrolyte.

4·2 *Thermodynamics of metal ion complex formation in solutions:* (B-3·4/67)

The β-diketones dibenzoylmethane and benzoylacetone are insoluble in water and hence, all experiments were done in mixed dioxane-water solutions containing 75 volume percent dioxane. The pH meter readings, (B) were converted to give the hydrogen ion concentration, $[H^+]$ by the expression.

$$-\log [H^+] = B + \log U_H^\circ - \log \frac{1}{\gamma_\pm}$$

where $\gamma_\pm$ is the mean activity coefficient and log U_{HO} is the correction factor independent of $\gamma_\pm$ but dependent on the mole fraction of dioxane and temperature. Its value is 75 volume % dioxane at any temperature, t °C, was found to obey the equation:

$$\log U_H^\circ = (0 \cdot 007406)\, t + 0 \cdot 828$$

The value of the thermodynamic ionization constants, the heats of ionization (ΔHi) and the entropy of ionization (ΔS_i), are summarized in the table :

Ligand	Medium	Thermodynamic ionization constants (Ki)			Heat of ionization (— Δ Hi)		Entropy of ionization (— ΔSi) cal./mole.
		15°C	25°C	40°C	Temp. co-efficient method K. Cal mole^{-1}	Calorimetric method K. Cal mole^{-1}	
Dibenzoyl-methane	75 volume percent dioxane + 25% water	13·9 ±·01	13·80±·01	13·80±·01	5·5±0·3	5·7±0·2	44±1
Benzoyl-acetone	—do—	12·89±·01	12·81±·01	12·70±·01	3·1±0·3	2·7±0·2	50±1
Anisoyl-acetone	—do—	13·26±·01	13·18±·01	13·05±·01	3·6±0·3	—	48·3±1
Acetyl-acetone	—do—	12·64±·01	12·58±·01	12·57±·01	1·2±0·3	1·3±0·2	53·3±1
Acetyl-acetone	Water	8·97±·01	8·88±·01	8·77±·01	3·2±0·3	—	30±1

5. THIN FILMS

In view of growing technological importance of metals, alloys and their chalogenide compounds in the thin film state, a detailed study on structural, optical and semi-conducting properties of these has been undertaken with a veiw to use the data in developing new devices.

5·1 *Structure of thin film :* (B-4·3/58)

The vapour phase deposits of Bi, Sb, Bi-Sb system, Sb$_2$Se$_3$, Sb$_2$Te$_3$ and oxidation process of Bi and Sb were studied by electron diffraction at various conditions of temperatures, pressures and substrates. The general nature of the growth process of crystals was similar irrespective of the differences between the structures of the deposits and of the substrates. Epitaxy was in general favoured at high temperatures.

The results in the case of Bi, Sb and Bi-Sb system were more or less similar from the point of view of the development of orientations. All these deposits were found to have hexagonal (rhombohedral) structures and no new phase change was noted. On rock salt (100) faces, these films developed

2-d $\{10\cdot2\}$ and 2-d $\{30\cdot7\}$ orientations. On the (110) faces, the orientation was 2-d $\{30\cdot\bar{1}4\}$, but Bi developed in addition 2-3 $\{\overline{11}\cdot0\}$ and $\{11\cdot\bar{7}\}$ orientation. On the octahedral face of rock salt, a mixture of 2-d $\{00\cdot1\}$ + 2-d $\{\overline{11}\cdot\bar{9}\}$ orientations was observed for Bi, Sb and Bi-Sb systems. On mica, Bi developed 2-d $\{00\cdot1\}$ orientation, whilst for Sb and Bi-Sb mostly 1-d$\{10\cdot2\}$ and $\{0\cdot1\cdot\bar{1}\}$ orientations were observed.

BiO (bismuth suboxide) was prepared and it had a f.c.c. structure with $a_0 = 5\cdot70$ Å. BiO deposits developed 2-d $\{100\}$ and 2-d $\{110\}$ orientations respectively on (100) and (110) faces of rock salt whilst 2-d $\{111\}$ orientation on mica.

Sb_2Te_3 was found to have hexagonal (rhombohedral) structure. The deposits of Sb_2Te_3 developed 2-d $\{0\cdot01\}$ + 2-d$\{00\cdot1\}$ + 2-d $\{\overline{33}\cdot4\}$ orientations on a (100) face of rock salt, while on the (110) and (111) faces of rock salt and also on cleaved faces of mica a 2-d $\{00\cdot1\}$ orientation was obtained. Thick deposits on glass as well as on mica produced a number of one-degree oriented crystallites. Sb_2Se_3, on the other hand, was found to have an orthorhombic structure and developed simultaneously 2-d $\{100\}$ + 2-d $\{110\}$ + 2-d $\{120\}$ + 2-d $\{230\}$ orientations on all the faces. But these crystallites formed on (100) and (111) faces were rotated by 90° and 60°. A new cubic phase change was noted at 350° with $a_0 \simeq 5\cdot84$ Å. On mica the patterns had a number of 2-d orientations and streaks were found due to lamillar nature of deposits.

5·2 *Physics of thin films :* (B-4·4/58)

A systematic study has also been undertaken on the optical properties of thin films deposited from vapour phase. A preliminary investigation on vacuum deposits of Se revealed that transmission (I/I_0) of these films gradually decreased not only with the increase of film thickness, but also with the change of wavelength of the visible region. An important observation made, so far not reported before, was that for a certain film thickness range transmisson (I/I_0) gradually increased instead of decreasing, ultimately reaching a value nearly in the region of 100% of (I/I_0), and later on this again slowly decreased further with increase of film thickness as expected. Similar trend was also observed for different wavelengths, though this trend gradually decreased with decrease of wavelength. Heat treatment of the film in vacuo below 100° also affected the (I/I_0) value.

Further studies on the semiconducting properties of other system like GaSb, Ga_2Te_3 and other compounds have also been made and the results have been evaluated.

6. CRYSTAL AND MOLECULAR STUDIES

6·1 *Crystallography:* (B-2·5/59)

Work has been continued on the precise structure determination of simple aromatic compounds.

The preliminary structures of *p*-nitrotoluene and *p*-toluic acid have been determined; their refinement is still in progress. The approximately planar molecules of *p*-nitrotoluene are packed in an orthorhombic unit cell of space group Pcab. *p*-Toluic acid molecules form dimers; these dimers are packed in a triclinic cell of space group $P_{\bar{1}}$.

The preliminary structure of *o*-monomethyl aminobenzoic acid has also been determined. The compound crystallizes in the monoclinic system, space group $P\frac{2_1}{c}$ *with 4 molecules/cell of dimensions:*

$$a = 8{\cdot}15\ \text{Å},\ b = 15{\cdot}09\ \text{Å},\ c = 7{\cdot}03\ \text{Å};\ \beta = 118{\cdot}3^\circ$$

The molecules form dimers. The refinement of the structure with the help of about 900 reflections is in progress.

Work has also been started on the structure analyses of 2-nitro 4-methyl benzoic acid and 2-nitro 5-methyl benzoic acid.

6·2 *Spectrochemical studies:* (B-5·1/63)

In continuation of the study of the infrared spectra of amino salicyclic acids, the 3 and 6 amino salicyclic acids have been synthesized. Their spectra along with those of their hydrochlorides and sodium salts and deuterated *derivatives show that these acids exist in the zwitterionic form in the solid* state.

In order to gain more information on the nature of the zwitterion structure of these compounds, the spectra of the three amino phenols and their various derivatives were analysed. The unusual absorptions in the NH and OH stretching regions (as many as 9 bands) in the *m* and *p*-amino phenols in the solid state seem to indicate the presence of zwitterionic forms.

Quantitative analysis of metals in the transition metal chelates of *o*-aminobenzene sulphonic acid has been carried out in order to ascertain their exact composition. An infrared analysis of the spectra in the frequency region 650-360 cm^{-1} (Caesium bromide prism) showed that the SO_3^- deformation modes also show variation with the metal ion though, not as well as the degenerate stretching modes. The metal ligand bands expected in this region could not be unambiguously located due to overlapping vibrations.

The identity of a compound formed by the radiolysis of aqueous solu tion of benzene was established as β-hydroxymucondialdelyde by a detailed study of its infrared spectrum as well as those of two of its derivatives. Infrared spectra of a few model compounds like hydroxy diphenyls and a derivative of hydroxy furfural have also been investigated in this connection.

7. SYNTHETIC INORGANIC CHEMISTRY

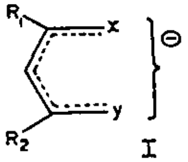
7·1 *Titanium and tin organics :* (AB-14/63)

Many reactions were carried out between lithium alkyls and various chelated titanium (IV) halides. Though, in most cases, the reaction proceeded smoothly (under nitrogen gas) with the separation of lithium halide, the expected sigma-bonded Ti-C type of compounds could not be isolated from the solutions either as such or as adduct with a donor molecule (pyridine). Even with the solutions, the Gilman test was negative. Products isolated from these highly moisture-sensitive solutions were often impure, and showed evidence of disruption of the chelate from the original reactant molecule.

Studies on the possible synthesis of alkyl tin halides by direct action of alkyl halides on the metal in presence of a catalyst led to a direct method of obtaining dibutyltin diiodide or oxide (Ind. Pat. No. 117210). The oxide reacts easily with organic acids to form the corresponding acylates. Chelated titanium (IV) dibutoxides reacted with it to form the expected Sn-O-Ti type of organics. Other similar compounds have been also prepared from triphenyltin hydroxide.

7·2 *Coordination compounds :* (B-6/63)

The conjugated monoanionic β-difunctional ligand shown in general form (I) is among the most fundamental chelating systems in coordination chemistry. In the last few years, general investigations were undertaken on the synthesis and stereochemistry of *bis*-chelate and *tris*-chelates complexes derived from (I).



I

An integral part of the work has been the study of the reactivity of acetylacetone and acetoacetanilide coordinated to a metal atom with various reagents. The structure of the complexes has been investigated by a variety of physical techniques; in particular IR and NMR spectra have been used to identify the substituted groups present and to assign structures to the complexes isolated.

In continuation of the work on the reactivity of the chelated ligands, reactions of *bis* (salicylaldehydato) copper (II) have been carried out. Nitration of *bis* (salicylaldehydato) copper (II) with copper nitrate trihydrate in acetic anhydride medium gave *bis* (3-nitro or 5-nitro-salicylaldehydato) copper (II). In addition, a brown resinous product was also obtained. Infrared spectrum of the nitro compound showed characteristic nitro group absorption at ca. 1550 cm^{-1}.

Bromination of *bis* (salicylaldehydato) copper (II) with N-bromosuccinimide gave a product which from elemental analysis and infrared spectrum was found to correspond to copper chelate of 3- or 5-bromo salicylaldehyde.

By the reaction of hydrazine hydrate with *bis* (salicylaldehydato) copper (II), *bis* (salicyladlehyde hydrazonato) copper (II) was isolated. Reaction of *bis* (salicyladehydato) copper (II) with salicyloyl hydrazide gave the anhydrous copper complex of salicylaldehyde salicyloylhydrazone (a tridentate ligand). *Bis* (β-resorcylaldehydato) copper (II) on reaction with hydroxylamine led to *bis* (β-resorcylaldoximato) copper (II) which on acetylation gave a new complex of copper with acetylresorcinaldoxime. The latter is an example of the reactivity of hydroxyl groups in the coordinated ligand whose coordination is so strong that the complex did not undergo decomposition.

In recent years, cyclopentadienyl-metal complexes, particularly cyclopentadienyl-titanium complexes, have attracted much attention for their applications in various fields such as catalysts, antiknock additives in motor fuels, thin film deposition of metals etc. Work on such compounds is, therefore, being carried out in this laboratory. Reactions of *bis* (cyclopentadienyl) titanium dichloride with various organic ligands are being studied. Direct reactions with acetylacetone and benzoylacetone proceed only partially yielding products which are difficult to purify. Rapid and complete reactions have been found to occur with the thallium (I) salts of these ligands, both the chlorine atom of the dichloride compound undergoing replacement. However, isolation of the compounds (C_2H_5) TiL_2 (LH = acetylacetone or benzoylacetone) could not be achieved due to their unstable nature. Reactions were carried out also with S-containing ligands, namely, thiosalicylic acid, thioglycolic acid, 2-mercaptopropionic acid, ethane-1,2-dithiol, 2·3-dimercaptopropanol, mercaptoethylamine, diethylaminoethane thiol and cysteine. All these ligands have been found to undergo rapid reactions in presence of ammonia, giving ammonium chloride as one of the products of reaction. Stable compounds having the formulation $(C_5H_5)_2$ TiL, where LH_2=thiosalicylic acid and ethane-l, 2-dithiol, have been isolated for the first time and characterized by IR, NMR and mass spectral studies. Reactions with thioglycolic acid, 2,3-dimercapto propanol and mercaptoethylamine gave insoluble and unstable titanium complexes which were difficult to purify. Titanium complexes obtained from the reactions with 3-mercaptopropionic acid and cysteine are under study.

7·2·1 *Metal dye complexes :* Since Alizarin Red S occupies an important position in the list of the acid-mordant dyes for wool and silk, investigations of the compositions of metal-dye complexes were undertaken.

Water soluble deep violet chromium (III) and copper (II) complexes of Alizarin Red S were isolated and their analytical and IR spectral data were recorded. The shift of 1660 cm^{-1} band of Alizarin Red S to lower frequencies in the complexes (Cu-complex, 1636 cm^{-1} and Cr-complex 1630 cm^{-1}) seems to indicate the involvement of the carbonyl group (9-CO) in complex formation.

7·2·2 *Spectral studies :* The IR, NMR and mass spectral studies supported the formulations for the thiosalicylato and ethane-1, 2-dithiolato compounds of *bis* (cyclopentadienyl) titanium. Molecular ion peaks recorded in the mass spectra confirmed the compounds to be monomeric with closed ring structures. Fragmentation process is being studied. Mass spectral study of similar and other cyclopentadienyl metal compounds is being pursued.

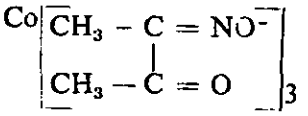
7·3 *Fluorine chemistry :* (AB-15/63)

The (trifluoromethyl) phenyl mercuric chlorides obtained by mercurating benzotrifluoride contain mono as well as dimercurated compounds. A successful attempt has been made to separate the mono mercurated product from the dimercurated by subliming the crude mixture in vacuum at 100-120°. It has been found that only 20% of the mixture gets sublimed which is purely a monomercurated compound. As usual, the sublimate and the unsublimable are converted into bromobenzotrifluorides which are then analysed by VPC, IR and NMR. These analyses revealed that the sublimate is *m*-chloromercuribenzotrifluoride. The unsublimable product is a mixture of two isomeric dimercurated compounds, 93% of one component and 7% of the other. The preponderant isomer of these viz., 93% is identified as 3,5-*bis*-chloromercuribenzotrifluoride. The identification of the 7% isomer is under progress.

8. PHYSICO ANALYTICAL CHEMISTRY

8·1 *New reactions of analytical importance :* (AB-16/66)

8·1·1 *Ligands of transition metal ions :* The interesting colour reactions of diacetyl monoxime with molybdenum and rhenium in their lower oxidation states were reported earlier. It is now observed that other transition metal ions such as those of nickel, copper, palladium and cobalt also react with this ligand in aqueous medium. The orange cobalt complex is also extractable into organic solvents such as benzene, chloroform and carbon tetrachloride. However, the red crystalline salt isolated from the organic extract is a diamagnetic chelate with cobalt in its trivalent state. It has the chemical composition $CoC_{12}H_{18}O_6N_3$ with the empiri cal formula



$$Co\left[\begin{array}{l} CH_3 - C = NO^- \\ \qquad\ | \\ CH_3 - C = O \end{array}\right]_3$$

8·1·2 *Sulphosalicylic acid in analytical chemistry :* Mn^{+2} in sulphosalicylic acid is rapidly air-oxidized to Mn^{+3} at pH over 9 to a deep brown Mn^{+3} complex. A mixture of Mn^{+2} and Mn^{+3} in alkaline sulpho-salicylate gives a reversible and composite anodic-cathodic polarogram. The Mn^{+2} complex is further reduced reversibly to the amalgam at a more negative potential. From polarographic data the formation constant of the 1:1 Mn^{+2} complex and the 1:2 Mn^{+3} complex have been estimated as log K = 5·2 and 20·5 respectively.

Advantage has been taken of the difference in stability between the sulphosalicylate complexes of Mn^{+3} and Fe^{+3} in working out an elegant method of separation of manganese from iron by cation exchange elution.

8·1·3 *Polarographic reduction of coordinated ligands :* The polarographic reduction of a metal coordinated to a ligand is largely dependent on the bond strength between the metal and the ligand, provided specific adsorption and catalytic phenomena associated with the d.m.e. do not intervene. However, no precise information is available as to what factors affect the E 1/2 of reduction of a ligand coordinated to a metal. A systematic investigation in this regard reveals that ligands may be broadly classified under two types: (a) those showing a negative shift in E 1/2 on coordination and (b) those showing a positive shift in E 1/2 on coordination. Among examples of the former class are α-nitroso-β-naphthol, nitroso-R-salt, coordinating azo groups dipyridyl. Oximes, rhodizonic acid and murexide fall in the latter class. It is interesting that in all the ligands of the second category (positive shift) the donor atom is linked to a carbon atom through a double bond where the double bond also undergoes reduction. Where the donor atom is not linked to carbon in this fashion, the negative shift is observed. The ΔE 1/2 in such negative shifts appears to increase with the strength of the chelate bond.

9. NATURAL ORGANIC PRODUCTS

9·1 *Utilization of β-himachalene :* (AB-17/67)

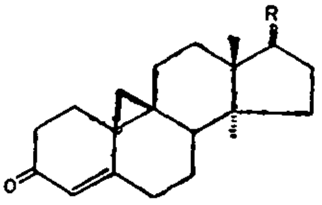
β-Himachalene is a major constituent of the easily available Indian deodar oil (*Cedrus deodara* Loud). Work to ascertain its utilization for preparing compounds of commercial value included (i) pyrolysis of β-himachalene and separation and characterization of the products of this reaction, (ii) preparation of the oxide of β-himachalene. Experimental work on both the aspects is in progress.

9·2 *Celastrus paniculatus :* (AB-18/67)

The Reproductive Physiology Unit, G. S. Medical College, Bombay, has confirmed that the total polyester fraction, isolated from *Celastrus paniculatus*, possesses valuable antifertility activity. A sample of tetracetate of one of the parent polyalcohols was prepared and has been supplied for testing its pharmacological properties. Work on the structure elucidation of the individual polyesters is being continued.

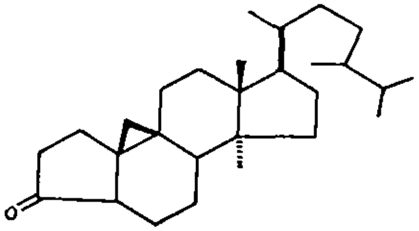
9·3 *Utilization of bye-products of opium alkaloid industry :* (AB-21/67)

9·3·1 *Preparation of steroidal hormone analogue from cyclo-laudenol :* Cyclo-laudenol and cylco artenol (readily available from opium marc) seem to be a potentially valuable starting material for the preparation of 9,19-cyclo steroids (1a & 1b) which may have interesting physiological activity.



1a: R; = O

1b; R: $-\underset{\underset{O}{\|}}{C}-CH_3$



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Work on the modification of side chain to C_{17}-methyl ketone is progressing satisfactorily. This work has also led to the development of an efficient and new method for the decomposition of ozomides.

Work pertaining to ring A modification is being carried out on cyclolaudenol. It has been degraded to compound (2) and all the intermediate products identified.

9·3·2 *Conversion of thebaine into codeine :* (AB-21/67)—Thebaine, which is obtained as a bye-product in the manufacture of morphine from opium, is not used in medicine. Conversion of thebaine into codeine can be achieved in two steps. Procedure for the first step i.e., thebaine to codeinone has been standardized. Experiments for the conversion of codeinone into codeine are in progress.

9·4 *Oleoresins and resinoids :* (B-7·1/67)

Work has been initiated on *Comniphora mukul*, a gum oleoresin of some medicinal importance. The neutral part of the resin has been taken up for investigation . Preliminary studies indicate it to be a rather complex mixture. From the saponifiable material a crystalline compound has been separated and identified as ferulic acid.

9·5 *Chemical investigation of Shouwia arabica :* (AB-63/68)

The recent prevalence of cattle jaundice (yellow disease) in Maharashtra, has often been associated with the consumption by cattle of the *Shouwia arabica* plant which grows wild in several regions of the State. This plant is a native of Egypt and might have entered India along with the cotton seeds imported from Egypt.

The problem was first referred by the Botanical Survey of India. Preliminary feeding experiments on rabbits and guinea pigs, conducted by the Animal Husbandry Directorate of the Maharashtra State, also indicated the poisonous nature of the plant.

From both leaves as well as the stem of the plant, a colourless crystalline product $C_{28}H_{56}O_2$, m.p. 86° has been isolated, which showed the presence of a carbonyl function.

A large quantity of potassium chloride (less than 1·5%) containing traces of Mn, Mg, Cu, Si, Na, Fe, Sn, Al, V, Ti and Ca has been isolated from the methanol extractive of the stem of the plant.

9·6 *Mucopolysaccharides :* (AB-64/68)

This work is being carried out in collaboration with B. J. Medical

College, Poona. Several cases of mucopolysaccharidoisis have been detected in children in Poona region which cause gross mental deficiency and retarded physical growth. Early diagnosis and treatment can save these children. The diagnosis would require the identification of the mucopolysaccharide in the urine and blood of the patients. No satisfactory simple procedure for its identification is available so far.

Some progress has been made in this work by a successful ionophoretic separation and identification of the uronic acid component of the mucopolysaccharide present. Based on this, a simple and quick method has been developed to distinguish between the usual mucopolysaccharides, namely, chondroitin sulphates A and B, and keratosulphate, present in the cases mentioned earlier.

9·7 *Co-dextrinisation of some indigenous gums and other polysaccharides :* (AB-50/68)

Dextrinisation brings about interesting changes in the structure of a polysaccharide caused by partial degradation and *trans*-glycosidation reaction. The resulting products show profound changes in properties.

Co-dextrinisation of two carbohydrate polymers in different proportions lead to similar changes and properties of the end-products are often significantly different from a mixture of the two individually dextrinised products in the same proportions.

The object of this work is to transform some of the inferior indigenous gums, available in quantity, such as jeol (*Odina wodier*), babul (*Acacia arabica*) Ain (*Terminalia tomentosa*), etc., with starches (tamarind kernel powder, etc.,) and other similar polysaccharides, to products, which are likely to find industrial application as adhesives, beater additives and thickeners in pulp and paper industry and in textile processing and printing.

Some preliminary work on the project has been carried out. Further work has been planned and is pending the fabrication of a laboratory dextriniser and a humidity control chamber.

9·8 *Chemical examination of Vetivaria zizanoides :* (B-7·4/60)

A systematic chemical examination of vetiver oil (Moosanagar variety) has been undertaken. Two alcohols and two ketones have been isolated. The alcohols have been characterized as khusimol and isokhusimol earlier isolated from South Indian vetiver oil. A ketone has also been characterized as khusimone. The structure elucidation of a new ketone m.p. 53° is in progress. The structure of khusinol has been revised.

9·9 *Synthetic experiments on berberine alkaloids :* (B.-8·30/68)

A number of protoberberine alkaloids have been synthesized from isoquinoline-l-aldehyde. A synthesis of corydaline has been achieved by this convenient route. In the course of this work an interesting aryl migration during Pictet-Gams reaction has been observed for the first time leading to the synthesis of l-methyl-4-phenyl isoquinoline in a convenient way.

Norcorydaline has also been synthesized by folllowing the new approach developed earlier.

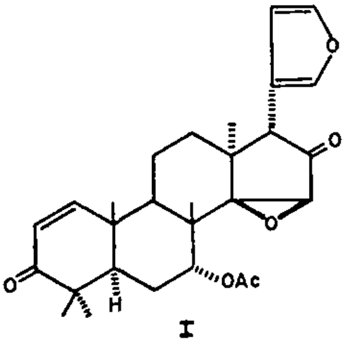
9·10 *Structure of salvin and picrosalvin :* (B-8·43/69)

The structure of two diterpenes, salvin and picrosalvin is known since long, but there was no clear evidence for their stereochemistry and absolute configuration. These have been achieved by interrelating them through chemical reactions and finding their relative and absolute stereochemistry by NMR and specific rotation studies.

9·11 *Nimbinin and related products :* (B-8·44/69)

Nimbinin is a minor product isolated from neem oil. This has been obtained in pure form and characterized as a tetranortriterpenoid. Its structure and stereochemistry has been determined as shown in (I), by chemical studies and physical measurements of the properties of the compound.

Another minor product occurring to the extent of only 0·003% has been isolated from neem oil and its structure and stereochemistry determined as shown in (II). This compound, vepinin is also found to be a tetranortriterpenoid and related to nimbin, the main crystalline constituent from neem oil.



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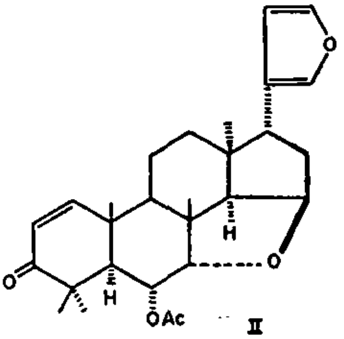

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Deacetyl-nimbin has been isolated and characterized as a natura product from the seeds and bark of *Azadirachta indica.* It has been shown by specific experiments that this is not an artefact produced during the isolation of nimbin.

9·12 *Conformational studies :* (B-8·45/69)

Primary hydroxyl groups in sesqui, di- and triterpenoids of rigid structure have been shown to have no free rotation but a preferred conformation. In case of the C_4-axial hydroxymethylene group this conformation has been shown to be the one in which the hydroxyl group nearly eclipses the C_4-equatorial methyl group. In the case of the C_4- equatorial hydroxymethylene group, it has been shown to be the one in which the hydroxyl group is 1, 3- diaxial with the C_3 axial proton.

In terpenoids of rigid structure it has been shown that carboxylic acid groups, their esters and aldehydes have no free rotation but assume preferred conformations. The conformation of the C_4-carboxyl group and its ester has been shown to be that in which the plane passing through the carboxyl carbon, carboxyl oxygen and the ether oxygen on it, is parallel to the plane passing through the C_2 and C_{10} carbons and the axial groups on them. In the case of the aldehydes, the conformation is that in which the conformation of the ester or acid is turned through 180°.

10. SYNTHETIC ORGANIC CHEMISTRY

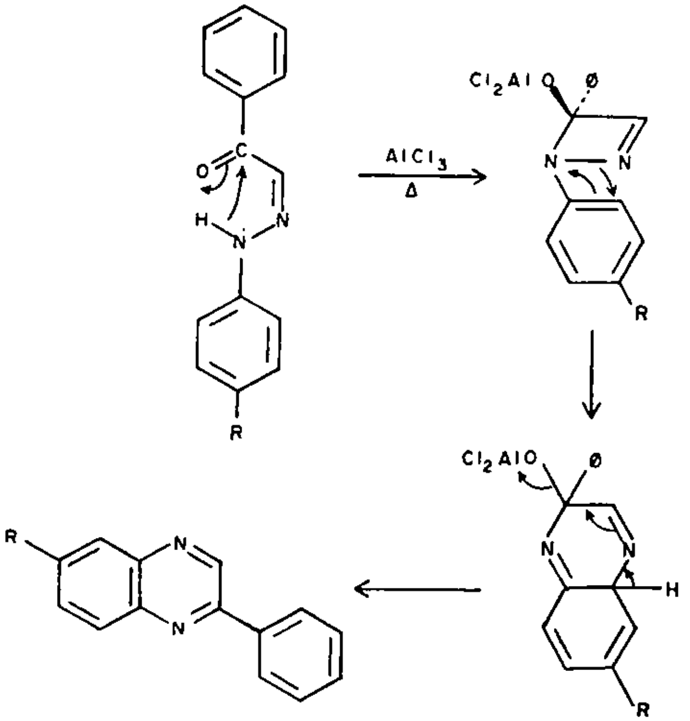
10·1 *4-Acetomethylcoumarins :* (B-8·3/66)

These studies were initiated to assign correct structure to the Kostanecki-Robinson acetylation products of orcacetophenone and its derivatives, which were earlier assigned the 4-acetomethylcoumarin structure.

NMR spectrum of the Kostanecki-Robinson acetylation product of orcacetophenone do not show the presence of the lone proton in the heterocyclic ring required by the acetomethyl coumarin structure. On the basis of spectral and chromatographic behaviour of these compounds and their degradation products, they have been assigned the alternative 2-methyl-3-acetylchromone structures.

10·2 *Synthetic studies in 4-arylcinnolines and 2-arylquinoxalines:* (B-8·4/64)

Cyclodehydration of the *cis*-isomer of phenylglyoxal-2-phenylhydrazones with molten $AlCl_3$-NaCl was found to give two isomeric products which were identified as 4-phenylcinnoline and 2-phenylquinoxaline respectively. The formation of the latter could be satisfactorily explained through a novel rearrangement postulating a diazetine intermediate, the reaction occurring in a concerted fashion.



R = H, CH$_3$ or Cl

Two isomeric N-oxides were obtained in each case when 4-phenylcinnoline and its 6-methyl and 6-chloro derivatives were oxidised with hydrogen peroxide in acetic acid. The isomeric 1-oxides and 2-oxides were separated and obtained in the pure form and their structures were determined on the basis of their NMR, IR, UV and mass spectral data.

10·3 *Transformation products of carvone and limonene :* (B-8·13/68)

Selective hydroboration of (+) limonene by disiamyl borane gave (+) *p*-menthane-6-ene-9-ol. The new asymmetric centre created at C_8 has been assigned the S-configuration by converting the above compound to (+) hexahydroturmerone and (+) β-(4-methylcyclohexyl) butanoic acid and comparing the rotation of the above compounds with that obtained from (+) *ar*-turmerone of known absolute stereochemistry.

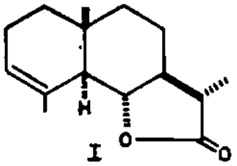
The hydroboration studies on limonene, carvone and its derivatives has been undertaken towards the total synthesis of natural zingiberene.

10·4 *Transformation products of costunolide:* (B-8·15/66)

Selenium dioxide oxidation of α-cyclodihydro costunolide (I), proceeds in an unusual manner, yielding a tertiary hydroxy lactone (II), even when a methylene and methyl groups in allylic positions, were available. The structure of (II) was established by spectral data and chemical reactions. Similar eudesmenic compounds with a double bond at C_3-C_4, undergo the same type of abnormal oxidation. β-Cyclodihydrocostunolide (III), the corresponding exocyclic double bond isomer, however, undergoes a normal oxidation, giving a secondary hydroxy-lactone (IV). On hydrogenation, (IV) gives 3- α-hydroxy santanolide 'a' (V), obtainable from (—) santonin.

The tetrahydrocostunolides (VI) and (VII) have been obtained in pure state from the partial hydrogenation products of dehydrocostunolide and their structures established by spectral data and chemical reactions. The epoxide of (VII), however, is not identical with tetrahydroparthenolide, though the spectral properties resemble those of tetrahydroparthenolide.

Liquid dihydrocostunolide, on cyclisation with acetic and perchloric acids gives in 20-30% yield a mixture of α and β-cyclodehydrocostunolides (II and III).



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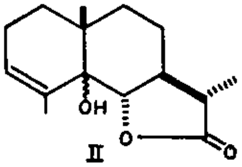

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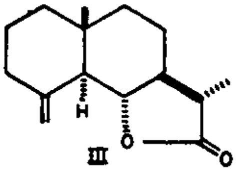

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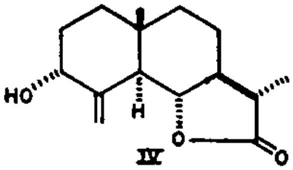

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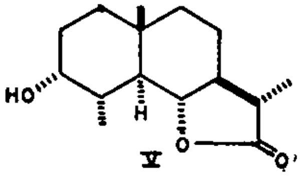

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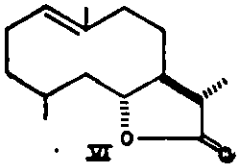

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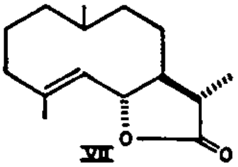


VII

10·5 *Synthesis of compounds related to selinane, elemane and p-menthane :* (B-8.16/67)

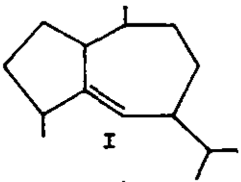
Compounds related to selinane and elemane are widely distributed in nature. One of the recent additions to this group is the tumour inhibitor, vernolepin. Total synthesis of β-elemene, elemol and tauremisin have been carried out.

Most of the work reported in literature on the synthesis of elemanic compounds involve the fission of the C_2-C_3 linkage of 3-oxoeudesmanes. A new approach has been made by carrying out the fission of C_3-C_4 linkage of 3-oxoeudesmanes and has been applied successfully for a synthesis of saussurea lactone.

10·6 *Chemical transformations of dehydrocostus lactone :* (B-8·19/65)

The hydrocarbons (I) and (II), obtainable from dehydrocostus lactone, as a mixture, have been separated into its components. Ozonolysis of (II), gave the keto ester (III) in about 80% purity. Selenium dioxide oxidation of (II) gave a mixture of conjugated ketone (IV) and alcohol (V) but it was not possible to isolate any of them in pure state. Jones chromic acid oxidation of the mixture of (IV) and (V) afforded an epoxy ketone (VI). The formation of (IV) and (VI), supports the structure (II) assigned to the hydrocarbon.

Dehydrocostus lactone, on treatment with formic acid gives a ctystalline formate lactone, whose structure is being studied by spectral data and chemical reactions.



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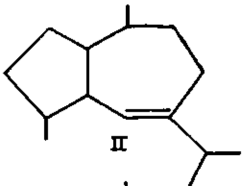

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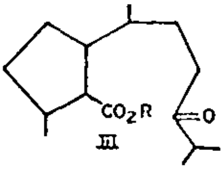

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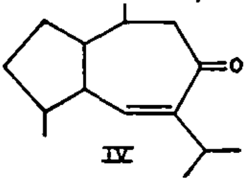

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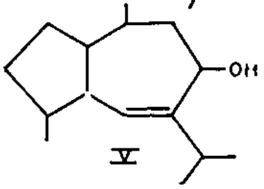

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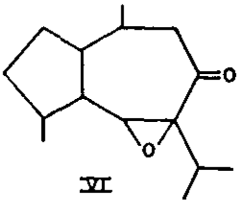


VI

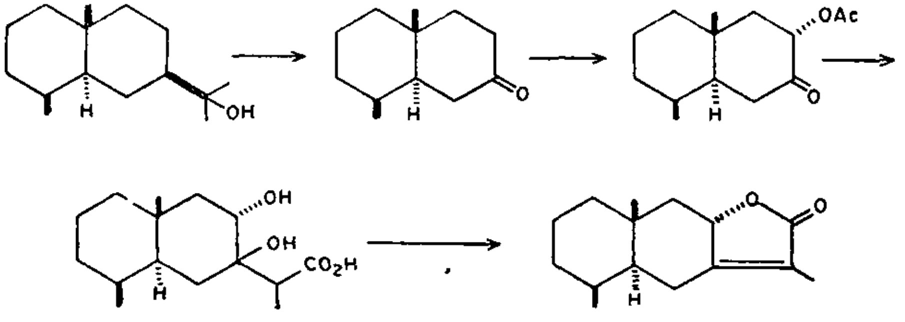
10·7 *Synthesis of sarkomycin:* (B-8·26/68)

Sarkomycin causes specific destruction of tumour cells and a preparation of this substance is marketted in Japan as a prescription drug against cancer.

Some of the intermediates required for a new synthesis of sarkomycin have been prepared.

10·8 *Transformation products of eudesmol:* (B-8·27/68)

Dihydroeudesmol has been converted to the lactone of 8-α-hydroxy-7(11)-ene-13-oic acid by the following series of reactions.



The above work has undertaken to correlate eudesmol to natural products. Thus the above lactone has been obtained from natural products atractylon and lindestrene thus establishing the stereochemistry at C_4, C_5, C_8 and C_{10}.

10·9 *Flavonoids* : (B-8.9/58)

The structure (5-hydroxy-3, 6, 8, 3′, 4′, 5′-hexamethoxyflavone) assigned earlier to gardenin (now called gardenin A), the flavonoid pigment of the resionous exudate of *Gardenia lucida*, is erroneous. NMR and mass spectral data have shown that gardenin has the structure 5-hydroxy-6, 7, 8, 3′, 4′, 5′-hexamethoxyflavone, confirmed by the isolation of 2-hydroxy-3, 4, 5, 6-tetramethoxyacetophenone and trimethylgallic acid as products of alkaline hydrolysis.

Gardenin A is accompanied by four other flavones (gardenin B, C, D and E). All the four flavones have the same A-ring substitution as gardenin A as shown by their mass spectra. Gardenin B is identical with the known 5-demethyltangeretin. Gardenin D is the 3′, 5′-dihydroxy-4′-methoxyderivative; C and E are probably the 3′-hydroxy-4′-methoxy, 3′-hydroxy-4′, 5′-dimethoxy derivatives.

A flavone having three isoprenoid units has been isolated from the bark of *Artocarpus heterophyllus.*

10·10 *Naturally occurring anthraquinone pigments :* (B-8·10/64)

10·10·1 *Synthesis of kermesic acid:* The structure of kermesic acid (*Tetrahedron Letters* 2223, 1968) has been confirmed by synthesis, starting from the anhydride of cochinellic acid methyl ether and hydroquinone dimethyl ether; but the synthesis does not distinguish between 1, 2, 4 and 1, 3, 4 substitution of hydroxyl groups in one ring.

10·10·2 *Synthesis of the methyl ether-ester of ceroalbolinic acid :* Condensation of the anhydride of cochinellic acid methyl ether and 1, 2, 3-trimethoxybenzene yielded a mixture of products which were methylated. Separation of the ether-esters led to two products, one of which was identical with the ether ester of ceroalbolinic acid.

10·11 *NMR spectra of anthrones :* (B-8·34/68)

The NMR spectra of very few hydroxyanthrones have been studied; but they are useful in determining the orientation of hydroxyl groups in naturally occurring anthraquinone pigments such as desoxyerythrolaccin. The structure of desoxyerythrolaccin has been shown to be 3, 6, 8-trihydroxyl-l-methylanthraquinone and confirmed by its synthesis in which isomeric products can be formed, but only one is normally expected by analogy as well as by reaction mechanism. The main problem is to distinguish between hydroxyl groups in the 5, 7 -and 6,8-positions. When a hydroxyanthraquinone in which only one carbonyl group is chelated with a hydroxyl, is reduced with stannous chloride and hydrochloric acid, the unchelated carbonyl undergoes reduction. The NMR spectrum of the resultant anthrone then clearly shows the diamagnetic shift of the α-protons adjacent to the methylene group. α-Hydroxyanthraquinone, xanthopurpurin and desoxyerythrolaccin were, thus, reduced to the corresponding 9-anthrones, the NMR spectra of which were determined. The structure assigned to desoxyerythrolaccin was confirmed by the diamagnetic shift of the 4,5-protons. The orientation of the substituents in kermesic acid follows, because kermesic acid has been converted earlier to desoxyerythrolaccin trimethyl ether by a series of reactions. Carminic acid and the laccaic acids will be investigated similarly.

10·12 *Zinc dust distillation of hydroxy anthraquinones carrying methyl groups :* (B-8·35/68)

The fact that 8-methylanthraquinone was isolated from the products of zinc dust distillation of erythrolaccin led to an erroneous structure, and NMR spectroscopy showed that the methyl group is in an α-position (*Tetrahedron Letters* 2231, 1968). Such migration of a methyl group has been observed in 4-methylalizarin. Zinc dust distillation yielded 8-methylanthracene as the major product; accompanied by traces of ∝-methylanthracene. Methods of desoxygenation which may not result in the migration of ∝-methyl groups are being examined.

10·13 *Tetrahydroxyanthraquinones :* (B-8·36/68)

In connection with the structures of laccaic, kermesic and carminic acids, it was necessary to examine the colour reactions and spectral properties of 1, 2, 4-6-and 1, 2, 4, 7-tetrahydroxyanthraquinone. In the course of this work, it was found that boron trifluoride etherate is a useful condensating agent for 4-chlorophthalic anhydride and 4-methoxyphthalic anhydride and behave differently in the condensation with 2-methoxyhydroquinone. The products ultimately led to the two desired tetrahydroxyanthraquinones.

10·14 *Synthesis of colucidin :* (B-8·37/68)

Colucidin is the aglycone of colucin, the 6-primeveroside of 1, 3, 6-trihydroxy-2-methylanthraquinone occurring in *Coprosma lucida* (L. H. Briggs). Colucidin has been synthesised by the condensation of 4-chlorophthalic anhydride and 2-methylhydroquinone in presence of boron trifluoride etherate, followed by a series of reactions.

10·15 *Studies in synthetic dyes*

10·15·1 *The Kolbe-Schmitt reaction on 2-hydroxycarbazole:* (B-8·38/68)-It has generally been assumed that carboxylation of 2-hydroxycarbazole under the Kolbe-Schmitt conditions yields mainly 2-hydroxycarbazole-3-carboxylic acid, used for the manufacture of naphthol AS-LB. The NMR spectrum of the commercial naphthol indicated that it is derived from 2-hydroxy-carbazole-l-carboxylic acid, and not from the 2,3-isomer. NMR spectral analysis of a mixture of the isomeric acids, which was made available by the M/s Bayer India Ltd., Bombay, indicated the presence in equal proportions of the 2, 1-and 2, 3 - isomers. The 2, 3 -isomer can be obtained from the mixture by repeated crystallisation from ethanol.

2-Hydroxycarbazole on treatment with BF_3-acetic acid complex at 100° gave mainly 2-hydroxy-3-acetylcarbazole (70%), together with the 2, 1-isomer (30%). Alkali fusion of the former yielded the 2, 3-acid.

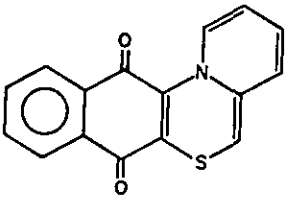
The orientation of the products by other reactions on 2-hydroxycarbazole is being studied.

10·15·2 *Leuco derivatives of vat dyes :* (B-8·39/68)—The sodium salts of the sulphuric esters of leuco derivatives of vat dyes dissolved in dimethylacetamide or tetramethylurea can be used for the determination of NMR spectra and then for investigating structural problems.

10·15·3 *2-Arylanthraquinones :* (B-8·40/68)—Work on the synthesis of 2-arylanthraquinones has been continued both from the point of view of the mechanism of the reactions involved and the possibililty of obitaining useful dyes.

10·15·4 *Heterocyclic vat dyes :* (B-8·21/68)—In continuation of the previous report, where the synthesis of hitherto unreported 3,4 -phthaloyl-2-thiaquinolizine (I) ring system was mentioned,the mechanism of its formation has been elucidated. While the action of mercaptomethylpyridine on 2,3-dichloro-1,4-naphthoquinone gave a disubstituted derivative as the main product under a variety of conditons, interaction of the above with 1,4-naphthoquinone led to a monosubstituted derivative as the major product. The latter, on cyclisation in presence of an external hydride abstractor gave (I). This study was then extended to the quinoline series. Thus, mercaptomethylisoquinoline was reacted with 1,4-naphthoquinone and the product cyclised whereby the thiaquinolizine (II) was obtained. The preparation of quinoline analogue is in progress.

The properties and chemistry of these new chromophoric-systems (I and II) are being examined.



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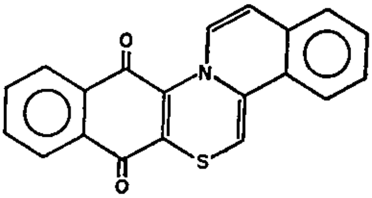

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10·15·5 *Indanthrene vat dyes :* (B-8·41/68)—The cyclisation of the Scholl type whereby two aryl nucleii are linked by a dehydrogenative process in presence of Lewis acids leading to the formation of a cyclic structure may proceed through a dihydro derivative of the anthrimide-carbazole or its derivative where two benzoylamido groups have undergone cyclisation with adjacent protonated carbonyl functions. This hypothesis is being examined in the case of cyclisation of 4,4′ -dibenzamido-1,1′ -dianthrimide which yields on cyclisation, the commercially useful vat dye, Indanthrene Olive R.

The cyclisation of 1-benzamide anthraquinone, 1,5-dibenzamidoanthraquinone, 1, N-diethylaminoanthraquinone and 4,4′- dibenzamidoanthraquinone with pyridines and acetic anhydride did not, however, yield a cyclic anthrone derivative under a variety of conditions as reported by some Russian workers (Fokin *et al.*). The formation of carbazole from anthrimide *via* the above mechanism involving cyclised intermediates, thus, appears improbable.

10·15·6 *Studies on reduction of quinones :* (B-8·20/68)—The alkaline hyposulphite reduction of anthrimides under certain conditons led to various reduction products following the initial reduction of the quinone to the leuco (hydroquinone) derivative. At the end of this reaction, the entire product was found to be unvattable indicating the absence of a quinone function. About 40% of the reduced material could be resolved into crystalline fractions (yellow needles 6%; green needles 18% and violet needles 16%) by preparative chromatography on silica gel. The structure of these compounds is under investigation employing spectral methods. Several model compounds are also being prepared in this connection, to study their reaction behaviour in alkaline hydrosulphite solution. It is believed that the alkaline hydrosulphite reduction proceeds through a free radical mechanism. It is also proposed to extend this study to various substituted anthrimides.

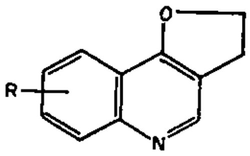
10·15·7 *Reactive dyes :* (B-8·42/68)—Technical preparation of five reactive dyes derived from cyanuric chloride has been standardized. A sixth example is one with copper phthalocyanine as the chromophore and β-chloroethylamino group as the reactive linkage. It is proposed to study the reactivity of the various reactive dyes towards cellulose fibre. New reactive dyes will be prepared by keeping the chromophore constant and changing only the reactive group. The effect on dyeing and various fastness properties by change of reactive function will be evaluated.

10·16 *Studies in heterocyclic compounds*

10·16·1 *Studies in hydride transfer reactions :* (B-8·7/65)—The work on the stereochemistry of hydride transfer reactions was further extended to the quinoline series. 1, 2-Dihydroquinolines are known to disproportionate in the presence of acid catalysts to yield quinolines and tetrahydroquinolines. The disproportionation involves intermolecular hydride transfer from one mole of dihydroquinoline to another molecule of protonated dihydroquinoline. It was of interest to study the stereochemistry of hydride transfer in the disproportionation of 3, 4-disubstituted 1, 2-dihydroquinolines. The latter compounds were, thus, disproportionated by interaction of polyphosphoric acid and the stereochemistry of the products was examined. A steric preference for the 3, 4-*cis*-disubstituted quinolines was observed. The hydride transfer process is affected by both steric and electronic factors. A tentative mechanism to account for the stereospecificity of the tetrahydroquinolines obtained has been proposed. With the view to study the anchimeric assistance offered by the nitrogen and sulphur atoms to hydride transfer to the conjugate acids derived from 1, 2-dihydroquinolines and Δ^3-thiachromenes, the solvolysis of tosylates of 3 and 4-1, 2, 3, 4-tetrahydroquinolines and tosylates of 3 and 4-thiachromanols will be studied. The relevant tosylates are being synthesized.

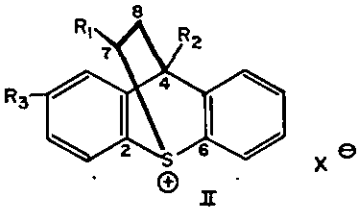
The preparation of 1,2 -dihydroquinoline derivatives is difficult because of the instability. A convenient synthesis of 1, 2-dihydroquinolines has been developed and the chemistry of these compounds has been studied. 1,2-Dihydroquinolines are facile hydride donors which are capable of effecting the reduction of carbon tetrachloride to chloroform and methyl iodide to methane. The mechanism of the reduction has been studied by spectral methods and also by deuterium labelling experiments.

The work on the stereochemistry of hydride transfer reactions is being extened to various heterocyclic systems containing two heteroatoms. Thus, a series of hitherto unreported angular 2, 3-dihydrofuro-(3, 2-c)—quinolines (I) have been synthesized and their reduction by hydride donors will be studied. Aromatization of (I) is also under investigation.



I

10·16·2 *Synthesis of compounds with potential biological activity :* (B-8·31/68)—In continuation of the studies on the synthesis of compounds having potential biological activity, substituted 9, 10-dihydro-10-thiaxanthenyl-9-acetic acids were prepared.



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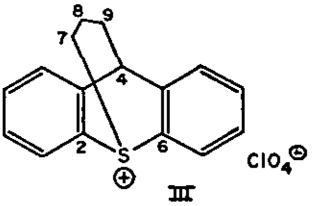


III

IIa $X = ClO_4^-$ $R_1 = R_2 = R_3 = H$

IIb ,, $R_1 = C_2H_5, R_2 = R_3 = H$

IIc ,, $R_1 = R_2 = H, R_3 = OCH_3$

IId $X = I_3^-$ $R_1 = R_2 = R_3 = H$

IIe ,, $R_1 = C_2H_5, R_2 = R_3 = H$

IIf ,, $R_1 = R_3 = H, R_2 = CH_3$

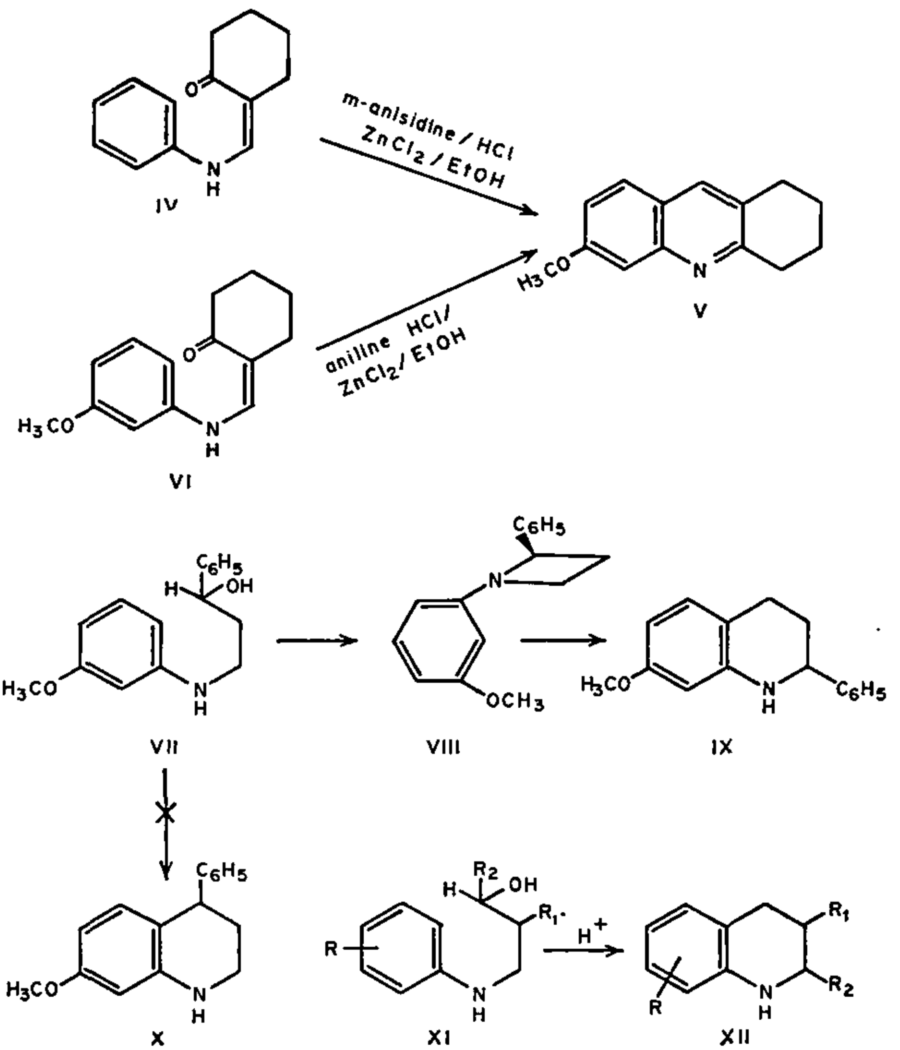
Lithium aluminium hydride reduction of these acids and in one case of the higher homologue obtained by the Ardnt-Eistert reaction gave the relevant carbinols which on cyclisation yielded the following: 2, 3, 5, 6 -dibenzo-l-thiabicyclo (2, 2, 2) octadiene (IIa-IIf) and 2, 3, 5, 6-dibenzo-l-thiabicyclo (2, 2, 3) nonadiene (III).

These compounds are being examined for their biological activity.

It was shown earlier, that 2-anilinomethyl- enecyclohexanone (IV) reacts with *m*-anisidine hydrochloride and $ZnCl_2$ in refluxing ethanol to yield 6-methoxy 1, 2, 3, 4-tetrahydroacridine (V). Similar reaction of *m*-anisidinomethylenecyclohexanone (VI) with aniline also gave (V). To study this reaction further, a series of *cis*-2-arylaminomethylenecyclohexanones were cyclised by interaction with different arylamine hydrochlorides, $ZnCl_2$ and other acidic reagents. It was observed that, whereas cyclisation of *cis*-2-arylaminomethylenecyclohexanones with polyphosphoric acid (PPA) gave the expected tetrahydrophenanthridines, interaction of these compounds with the above cyclodehydrating agents (including lactic acid) gave the rearranged tetrahydroacridines. The mechanism of formation of tetrahydroacridines which involves an interesting rearrangement is under investigation. It is likely that this rearrangement involves the intermediate formation of azetines which may be rearranging rapidly to the tetrahydroquinolines. In order to prove this hypothesis, the synthesis of azetidines was undertaken as a first step towards the synthesis of azetines. In one case, that of cyclodehydration of γ-*m*-anisidino - α-phenyl- α-propanol (VII), 2-phenyl-N-(*m*-methoxyphenyl)- azetine (VIII) has, infact, been isolated. The latter on keeping, rearranged to 7-methoxy-2-phenyl-1, 2, 3, 4-tetrahydroquinoline (IX). The normal product of cyclodehydration 4-phenyl-1, 2, 3, 4-tetrahydroquinoline (X) was not formed. Cyclodehydration of several other substituted arylaminoalkanols of the type (XI) under acidic conditions also give the rearranged products (2-aryl-1, 2, 3, 4-tetrahydroquinolines) (XII). A tentative mechanism for this rearrangement has been suggested. (See Chart I on page 85)

Cyclisation of 2-methyl-5-phenylamino-3-pentanol (XIII) and 2, 2- dimethyl-5-phenylamino-3-pentanol (XIV), by interaction with perchloric acid (70%) yielded 5, 5-dimethyl-2,3,4,5-tetrahydro-l-H-l-benzazepine (XV) and 4, 5,5- trimethyl-2, 3, 4, 5-tetrahydro-l-H-l- benzazepine (XVI), respectively, as major products. This cyclisation involves a carbonium ion rearrangement. When 5-*m*-anisidino-2, 2- dimethyl-2-pentanol (XVII) is catalysed under similar conditions it undergoes successive carbonium ion rearrangements leading to 4-isopropyl-7-methoxy-4-methyl-l, 2, 3, 4- tetrahydroquinoline (XVIII); various other substituted anilinopentanols (XIX) have been synthesized and cyclised under acid catalysis and the products obtained are being examined. (See Chart II on page 86)

CHART I

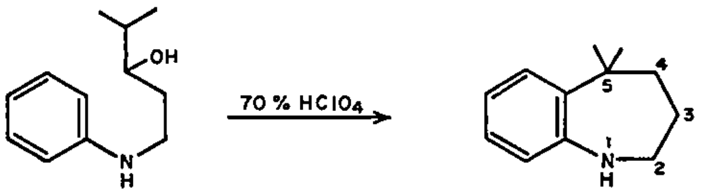


10·17 *Antifertility drugs:* (AB-25/66)

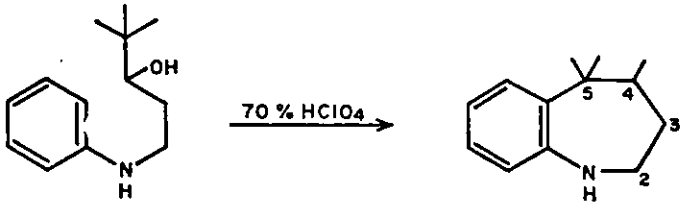
Attempts to synthesize the thiophene analogue of stilbestrol are being continued, but the work towards the synthesis of 11-thiasteroids has been temporarily suspended.

For the synthesis of 11-aza steroids the key intermediate 7-keto-3-methoxy-5-methyl-5, 6, 6a, 7, 8, 9, 10, 10a-octahydrophenanthridine (I) has been synthesized by a two step reduction of 3-methoxy-5-methyl-7-keto-7, 8, 9, 10-tetrahydrophenanthrinium iodide (II), followed by Oppeanauer oxidation. (See Fig. on page 86)

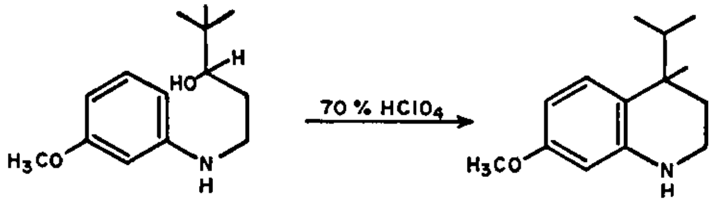
CHART II



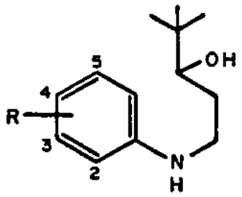
XIII XV



XIV XVI



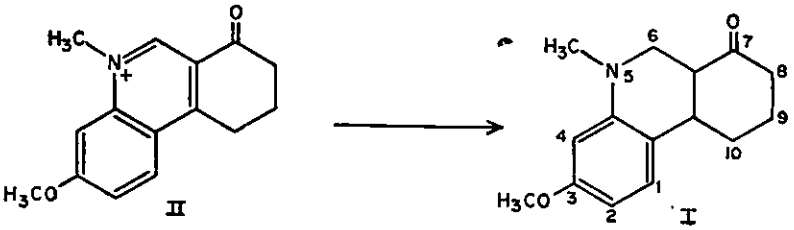
XVII XVIII



XIX

R = 2-OCH$_3$, 4-OCH$_3$, 2-CH$_3$
3-CH$_3$, 4-CH$_3$.

Antifertility drugs



11. PHYSICAL ORGANIC CHEMISTRY

11·1 *Mass spectrometry:* (B-5·7 & 5·8/65)

A structural tool: No systematic studies on correlating structure and fragmentation of sesquiterpenic lactones has been reported in literature. A detailed investigation on the fragmentation of some furanogermacranolides, germacranolides, guaianolides and pseudo guaianolides has been initiated. Deuteration and high resolution data were obtained to confirm the proposed fragmentation modes. It has been shown that mass spectrometry can be successfully used as a structural tool in sesquiterpene lactone chemistry. Part of this work has been published.

Multiple rearrangements induced by electron impact: Backmann and pinacol- pinacolone rearrangements induced by electron impact were studied in detail. Substituent effects, meta-stable ion characteristics and application of kinetic theory have been used to arrive at the structures of intermediate ions involved in these rearrangements. The structural requirements for electron impact induced pinacol-pinacolone rearrangement have been established. In the mass spectral fragmentation of anilides, some novel type of reorganization processes taking place under electron impact have been observed. The poor correlation between fragmentation modes and Hammett σ values of substituents, has been rationalized as due to competing fragmentation modes.

Mass spectra of organo-metallic compounds: In continuation of previous efforts to characterize organometallic compounds by mass spectrometry, some organophosphorus and silicon compounds have been examined. Many interesting fragmentation reactions have been observed which are being studied in detail.

Stereochemical studies: Comparative study on the behaviour of a number of bicyclo heptane derivatives under electron impact was made.

Fragmentation of heterocyclic compounds: It was observed that NMR data are not of much help in distinguishing cinnolines and quinoxalines. However, on the basis of their mass spectral fragmentation modes, these compounds could be successfully characterized. It has been shown that these sets of isomeric compounds can be distinguished and the position of substituents in the various rings located from their mass spectra.

The fragmentation of some benzophenanthridine derivatives was examined with a view to find out the influence of the position of the nitrogen atom on the fragmentation mode. The results have been published.

High resolution mass spectrometry: Work on standardizing the peak matching technique has been completed.

It is possible to compute elemental compositions from accurate masses obtained by peak matching technique. With this approach it was possible to arrive at elemental compositions of fragment ions in many sesquiterpene lactones and other natural products. Efforts have been made in the use of computer techniques in the interpretation of mass spectra.

11·2 *Studies on conjugated systems:* (B-5·2/62)

11·2·1 *Donor-acceptor interaction and hyperconjugation*

(a) *Long range spin-spin coupling and π-electron distribution:* An attempt has been made to see if donor-acceptor interaction can be studied by following changes in the long range coupling of methyl protons in systems like 6-substituted 3-nitrotoluenes and 5-substituted 2-nitrotoluenes. The results for the first series were of some help while those for the latter did not show any significant variation. Apparently, the methyl group itself acts as a donor in the latter system and the interaction of the acceptor group with the *p*-substituent is diminished.

(b) *Proton chemical shifts in benzene derivatives:* A new method for studying donor-acceptor interaction using nuclear magnetic resonance has been elaborated. The analyses of the spectra of the three spin systems have been refined by the method of computor simulation. It has been found that the chemical shifts of the C_3-and C_6-protons of 4-substituted phthalic esters show a systematic variation after correction for the 'normal' substituent effects. The corrected chemical shifts vary linearly with donor strength (σ_R) of the 4-substituent. The data for methyl and *t*-butyl derivatives can be rationalized best with the help of the concept of hyperconjugation.

Most of the preparatory work for the extension of this method to *o*-dinitrobenzene and *o*-nitrobenzoic acid derivatives has been completed.

(c) *Nucleophilic reactivity of o-dinitrobenzene derivatives:* One of the nitro groups of an *o*-dinitrobenzene can be readily replaced by groups like methoxide or hydroxide. The kinetics of this reaction has been taken up for study and rate measurements for four compounds at two temperatures have been completed. The measurements will have to be extended to one or two more temperatures for the computation of the Arrhenius parameters. Although the study is not yet complete, there are strong indications that the conclusions of the NMR and IR studies on the relative donor strengths of the methyl and *t*-butyl groups will be supported by the rate measurements.

11·2·2 *α-Proton chemical shifts in cyclohexanones :* If hyperconjugation is important in the ground state, the α-methylene and carbomyl groups of a cyclohexanone would form a conjugated system. A study of the chemical shifts of the α-methylene protons has been undertaken to see if conjugation is really important in this system. The preparation of suitable derivatives has been taken up and considerable progress has been made.

11·2·3 *Studies related to the Mills-Nixon effect :* The thioketal of 5-bromoindan-l-one has been prepared and its reaction with lithium piperidide investigated. The results are under evaluation.

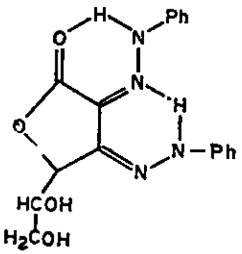
11·2·4 *Carbonium ions :* All attempts that have been made so far to prepare α-acetoxy-*p*-*t*-butylbenzyl perchlorate have given negative results. This is perhaps significant and the suggestion seems to be very strong that the ability of the *t*-butyl group to stabilise a carbonium ion is very much less than that of the methyl group.

The acetoxy-benzyl perchlorates are converted into benzylidene diacetates in acetic anhydride while they are unaffected in acetic acid or ethyl acetate. Acetic anhydride thus appears to be a more basic reagent than acetic acid or ethyl acetate towards the carbonium salts. The significance of this behaviour and its implications have been taken up for a detailed examination and a number of experiments have been done.

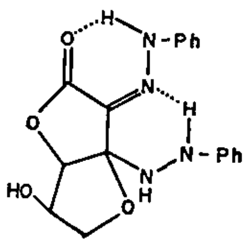
11·2·5 *Structural and stereochemical studies*

(a) *Structure and mutarotation of ascorbic acid osazone :* NMR spectra of ascorbic acid osazone in dimethylsulphoxide solution shows striking changes with time. These have been rationalized in terms of the 'mutarotation' of the osazone.

The osazone has so far been regarded as a γ-lactone. However, it has recently been claimed that NMR and IR spectra and also the chemical behaviour of the substance are in better accord with a δ-lactone structure. This structural question has been reinvestigated with the help of NMR spectra and it has been possible to show that the γ-lactone formulation is correct.



I



II

It has also been shown that the γ-lactone exists in two forms (I and II): which are interconvertible. The behaviour of the substance towards oxidizing agents and the cleavage of the oxidation product on treatment with alkali are quite readily rationalized in terms of the revised structural formulation.

Dehydroascorbic acid and ascorbic acid should give the same osazone. However, when the osazone preparation is done after oxidation of ascorbic acid with iodine the product obtained is found not to be the same as from the parent compound. The structure of this product is under study.

(b) *Conformation of 1,3-thiazane derivatives :* The NMR spectra of a series of 1, 3-thiazane derivatives (prepared at the BARC, Bombay) shows very interesting chemical shift changes with changes in substitution. An attempt is being made to see if the observations can be accounted for in terms of conformational factors.

11·2·6 *Electronic spectra*

(a) *Benzene derivatives :* Comparison of the electronic spectra of 2-nitro-4-methylaniline and the corresponding *t*-butyl derivative obtained in non-polar solvents suggests that the methyl group is a stronger electron donor than the *t*-butyl group. This order is the reverse of that found in the case of *p*-alkylnitrobenzenes. The significance of the observation is under study and it is proposed to examine a number of similar derivatives.

(b) *Theoretical calculations:* A computer programme for modified Hückel type calculations of π-electron energy levels in aromatic compounds as well as the associated transition probabilities is in preparation. Part of the programme in 'Fortran' has been completed.

11·2·7 *Long range coupling:* Long range coupling has been found to exist between benzylic protons on ortho-carbon atoms of a benzene ring held rigid in a cyclic system. The magnitude of this coupling across fine bonds is found to depend on the angle, these protons make with the plane of the benzene ring.

11·2·8 *Solvent effects :* Cyclic ethers and other heterocyclic compounds as those containing nitrogen and sulphur atoms are found to give different chemical shifts to protons depending on the location of the proton from the hetero-atom. A rule has been found to exist to predict these solvent shifts. In a rigid system, if a plane is drawn passing through the mid-points of the carbon oxygen bonds (or C-N or C-S bonds) and perpendicular to the plane made by the oxygen atom (sulphur or nitrogen as the case may be), and the two carbon atoms holding it, then protons lying in front of the plane (towards the oxygen atom) are deshielded and those lying behind the plane (away from the oxygen atom) are shielded. This rule would be of considerable importance in finding the structure and stereochemistry of unknown or partially known compounds.

Compounds containing methyl groups which have a 1,3-diaxial relation with a hydroxyl group can now be easily detected by a new solvent effect found with pyridine. If the NMR spectra of such compounds are determined in chloroform and pyridine solutions, the signal of the methyl group moves down about 10-16 cycles (at 60 Mc) in the spectra in pyridine solution, compared to that in chloroform. This would be of considerable use in determining the stereochemistry of methyl or hydroxyl groups in natural and synthetic products.

It is known that when a hydroxyl group is esterified the proton on the carbon, holding the hydroxyl group is deshielded. But there was no clear idea of the deshielding effect on other protons in the neighbourhood. This has now been determined by preparing a number of compounds in which the signal of the neighbouring protons can be identified and by finding their deshielding effect. The effect has been found to be very significant in the case of tertiary hydroxyl groups.

Many natural γ-lactones fused to prehydronaphthalene systems have a methyl group adjacent to the carbonyl group. There was no physical method and no simple chemical method to find the stereochemistry of this methyl group. As a result there was considerable confusion in the literature regarding the stereochemistry of this methyl group. Two simple methods have now been devised, one by solvent shifts in chloroform, benzene and pyridine, and another by coupling constants, to find directly the stereochemistry of this methyl group. This has been applied to about fifty γ-lactones and has been found to hold good. It has recently been used to find the stereochemistry at this point in several new γ-lactones.

12. MICROBIOLOGY

12·1 *National Collection of Industrial Microorganisms:* (AB-62/68)

Non-pathogenic microorganisms (yeast, bacteria and fungi) which are of importance in research and industry are maintained in this culture collection. Cultures are supplied free of charge on request to scientific institutions and industries. By supplying these cultures, which would otherwise have to be imported from abroad, a considerable saving in foreign exchange is effected. Identification of cultures obtained during screening programmes of microorganisms in the laboratory is routinely undertaken. Research on the preservation of cultures especially under paraffin oil, which is relatively simple and requires no specialized equipment, has also been in progress as a long term project.

The routine maintenance and subculturing of the microorganisms were carried out. The cultures were tested for their biochemical performance and those preserved under paraffin oil were tested for their viability. 612 cultures were despatched to different institutions.

12·2 *Production of mutants*

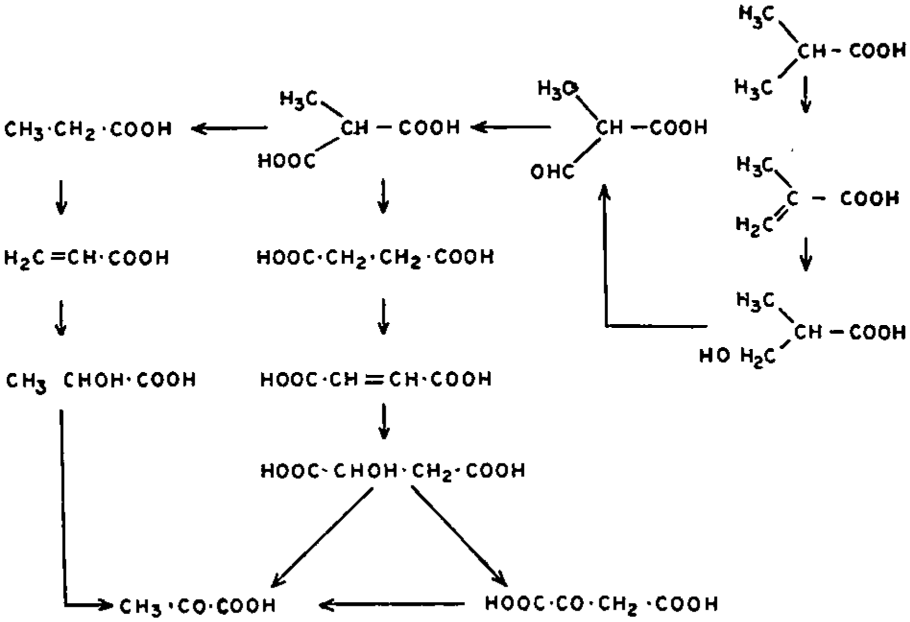
A few mutants of *Serratia marcescens* requiring glutamic acid, threonine and tryptophane have been isolated. The sites of biochemical lesion are being studied.

12·3 *Microbiological transformation of terpenes :* (B-10/59)

Microorganisms have been known for a long time to bring about useful chemical changes such as hydroxylation, hydration of a double bond, oxidation of a hydroxyl group, rupture of alicyclic rings and carbon-carbon bond cleavage. The present work is undertaken to convert easily available terpenoid hydrocarbons into oxygenated products of potential interest to the perfumery industry as well as to elucidate the biochemical mechanism underlying these transformations.

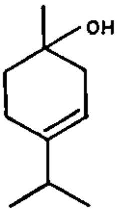
12·3·1 *Bacterial transformations :*

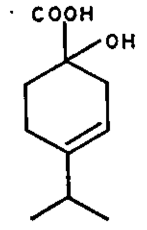
(a) *Terminal oxidation pattern of PL-strain :* Based on the growth and oxidation pattern of PL-strain on various suspected intermediates, the following alternate mechanisms have been proposed.



The next attempt was to identify the presence of the individual enzymes involved in this scheme. It has been possible to show a non-enzymatic conversion of methacrylic acid by following spectrophotometrically the change in the absorbance at 240 mμ. This may include also a possible enzymatic conversion which will at present be difficult to establish. However, the presence of an activating enzyme for isobutyric acid in the cell free extracts of PL-strain grown on isobutyrate has been identified and it has been further shown that ATP and coenzyme A are essential for the reaction. The probable presence of an enzyme activating succinate is also being indicated in the extracts. But whether these two activities are due to the different enzymes or due to one enzyme alone can be settled only after some extensive enzyme purification experiments.

(b) *Fermentation of* Δ^3-*p-menthene:* The PL-strain which has been adapted to grow on Δ^3-*p*-menthene was used in large scale fermentations in order to isolate and identify the products formed. The fermentation broth was subjected to the usual isolation and fractional procedures. The following compounds could be isolated in quantities sufficient for the conventional identification procedures using physico chemical techniques:


(1)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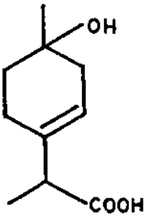
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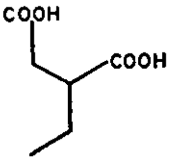
(4)

Compound number (4) could be identified as ethyl succinic acid whose identity was further confirmed by comparison with an authentic sample. The latter was synthesized using well-known method described in the literature. This work has now been completed.

13. GROWTH OF PLANT CELLS : (B-11/63)

The study of the growth and metabolism of different plant cells is of interest in connection with plant growth and the formation of useful plant products. The objectives of this long range project at present are: (i) to determine the requirements for rapid growth of different plant cells (ii) to study the growth of monocotyledonous cells and other plant tissues which have hitherto been investigated only to a limited extent and (iii) to study the metabolism of normal and tumour cells of plants. These studies on different plant tissues are of potential agricultural importance.

The requirements for the continuous growth *in vitro* of cells from different plants such as opium, cholai, maize etc., were determined. Twenty five plant cell cultures are being maintained at present of which some were isolated and established for the first time in this laboratory.

The nutritional requirements and the rates of growth under different conditions of maize, wheat, jowar and rice, which were found to be viable *in vitro*, were studied. The growth of all the cultures except rice was much more rapid in shake flasks than on solid media. The growth of maize was about 20 times faster under conditions of vigorous agitation than on agar. The rates of utilization of sucrose and phosphate and the effect of different hormones on the growth of maize under submerged conditions were determined. The effect of aeration, auxin, gibberellin and adenine on root formation was studied. A striking increase in root formation was observed in shake flasks or when the solid medium was supplemented with adenine or gibberellic acid in the presence of low levels of auxin.

Work on the isolation of different plant cell mutants and on compounds which selectively inhibit tumour cells is in progress.

14. ENZYMES

The study of enzymes is closely related to the study of intermediary metabolism. The work on enzymes is directed towards the isolation of enzymes and the study of regulatory mechanisms which control metabolism.

14·1 *Hexokinase* : (B-12·1/63)

Animal tissue hexokinases have not hitherto been obtained in pure form. A new method was developed for the solubilization of hexokinase from brain and heart. The enzyme from brain was obtained in a state of high purity and its properties were studied.

The insoluble hexokinase of heart was obtained in soluble form and purified about 500-fold. Its kinetics and properties were studied. This enzyme differed from the particulate enzyme of brain with regard to inhibition by glucose-6-phosphate. The glucose-6-phosphatase of liver was also obtained in a soluble and highly stable form. Different methods of purification which were tried however yielded only a slight increase in specific activity.

14·2 *Phytase* : (B-12·2/64)

A bacterial enzyme which specifically hydrolyses inositol hexaphosphate was discovered. Partial purification of the enzyme and the study of its specificity were carried out.

A new *B. subtilis* culture which produces phytase in large amounts was isolated. The enzyme was purified about 50-fold. Its application for the detection and estimation of phytate in biological materials is being investigated.

14·3 *DPNase :* (B-12·4/65)

The isonicotinic acid hydrazide-insensitive DPNases have been purified from animal tissues but the isonicotinic acid hydrazide sensitive enzyme from ox brain has not hitherto been obtained in purified form.

The enzyme from ox brain was obtained in soluble form and purified 400-fold. Enzyme of maximum purity was extremely unstable but could however be kept for several weeks without loss in activity in the presence of serum albumin. Its properties and kinetics are being studied.

14·4 *Acetylcholinesterase :* (B-12·3/64)

Acetylcholinesterase plays an important role in the metabolism of brain and nerve and has been obtained in soluble form and purified to a considerable extent from the electric organs of fish. A new method has been developed for the preparation of soluble acetylcholinesterase from ox brain.

Work on the purification and the study of properties of the enzyme was completed. The soluble enzyme was purified 5000-fold to yield a final preparation with a specific activity of about 100,000 μ moles of substrate hydrolysed/minute/mg. protein. This is the purest acetylcholinesterase obtained hitherto from brain. The inhibition of the enzyme by fluoride was noncompetitive whereas its inhibition by butyrylcholine, eserine and prostigmine was competitive. It showed a sharp substrate optimum with inhibition at higher concentrations of substrate, which is characteristic of true acetylcholinesterases. Several of its properties were also similar to those of the enzyme from electric cell. It showed a very low increase in activity with temperature and the activities at 30° and 37° were nearly the same. The enzyme was found to be rapidly and irreversibly inactivated when frozen in the presence of phosphate and thioethanol. There was no inactivation in the absence of either phosphate or thioethanol or when the enzyme was kept in the presence of the two substances at 0°. Phosphate could be replaced by pyrophosphate but not by any other anion whereas there was no inactivation when thioethanol was replaced by glutathione or cysteine. It was not possible to reactivate the enzyme by any of the procedures which were tried. The inactivation could be prevented by acetylcholine, EDTA or reduced glutathione.

14·5 *Acylphosphatase :* (B-12·7/68)

Acylphosphatases are known to occur in animal tissues. Their occurence in plants has not been investigated. Since acylphosphates do not occur in plant or animal tissues, the function of this enzyme and its role in the regulation of metabolism are obscure.

The acylphosphatase content of different plant materials was determined and *Vigna catjang*, which had the highest enzyme content, was used for the isolation of the enzyme. It was separated from ATPase and other non-specific phosphatases which were present in the seeds. Unlike ATPase, acylphosphatase was insensitive to fluoride. It showed no metal requirement and was not inhibited by *p*-chloromercuribenzoate or EDTA. The purification and the study of the properties of the enzyme are in progress.

14·6 *Metabolism of nitrate by Achromobacter fischeri :* (B-12·6/64)

Microorganisms play an important role in maintaining the nitrogen cycle. The activity of denitrifying bacteria accounts for substantial losses of nitrate containing fertilizers. Biochemical studies undertaken with whole cells and isolated enzyme systems will help understand the basic mechanisms involved in these denitrifications.

Nitrite reductase from *A. fischeri* has been obtained in a pure form. The heme moeity of the enzyme is not split by acid-acetone but is split off by treatment with silver sulphate as described in the literature. Molecular weight of nitrite reductase as determined by Sephadex G-200 filtration technique corresponds with the results obtained earlier by the Archibald's method.

With pure nitrite reductase and with reduced benzyl viologen or NADH as electron donor, the reaction product of nitrite reduction has been identified as ammonia. A stoichiometry of 6 moles of reduced benzyl viologen (or methyl viologen) or 3 moles of NADH (or NADPH) oxidized per mole of nitrite disappeared (or ammonia formed), has been found. This stoichiometry is not influenced by pH. Earlier studies with whole cells had indicated that one of the products of nitrite reduction was nitric oxide. This suggests that there are two different pathways of nitrite utilization by *A. fischeri*.

With pure nitrite reductase, the nitrite loss and ammonia production occur far more rapidly than the corresponding changes observed for hydroxylamine present at equivalent concentrations. This casts doubt on the status of hydroxylamine as a possible intermediate in the reduction of nitrite to ammonia.

The addition of a variety of protein denaturants, 4 M urea, 4 M guanidine hydrochloride or treatment with acid at pH 4·5 at 4° for 8 to 10 minutes inactivated the enzyme completely. The inactive protein can be reactivated almost fully having more than 90% of the activity of the native enzyme. The characteristics of inactivation and reactivation of the enzyme are being studied.

14·7 *Citrate-oxaloacetate lyase* (*Citrase*) *:* (B-12·5/65)

Mg^{2+} has been shown to play an important role in maintaining the subunit structure of the enzyme. In the presence of the metal ions, the enzyme exists only as dimers even in urea and guanidine hydrochloride systems.

The binding of oxaloacetate and acetate by the enzyme has been studied using C^{14} - labelled ligands.

A sensitive immunological test for citrase has been developed using specific rabbit antiserum. The antiserum has been applied to the detection of dissociation of the enzyme molecule.

14·8 *DFP-susceptible enzymes and antidotes :* (AB-65/68)

Disopropyl phosphorofluoridate (DFP) is the most important prototype of modern insecticides like parathion and the class of highly toxic chemical warfare agents like 'Sarin' and 'Tabun.' Biochemically, DFP is highly selective in its action, in being able to inhibit a class of hydrolytic enzymes which have a serine molecule at the active centre. The study of the mode of action of DFP in living cells is likely to yield data which may be useful in the better application of organophosphorus insecticides and in better methods of countering the toxic effects on humans and higher forms of life.

The effect of DFP at low concentrations (10^{-6} to 10^{-5}M) was studied on various plant tissues grown in culture media. There was a substantial reduction (20-30%) in the growth rate of maize, opium, parthinocissus, crown gall and other tissues if DFP was incorporated in the growth medium one or two weeks after inoculation. If the inoculum itself was initially treated with DFP, the growth rate was reduced to a greater extent (40-60%). An interesting observation was that in the pair parthinocissus normal and parthinocissus crown gall, only the tumour tissue was affected by DFP. Experiments are in progress to determine whether the action of DFP on the cell is quantal, of the all-or-none type, or whether the growth retardation is a graded response related to esterase inhibition in the inoculum.

Young mice protected with antidotes and then periodically administered 2 LD_{50} S of DFP did not show any reduction in the growth rate. The injection of DFP at one LD_{50} once, resulted in a statistically significant change in the K/Na ratio of the liver tissue. This change was not perceptible in animals protected with atropine and the oxime antidotes. The effect of DFP on the K and Na content of tissues has not been recorded previously.

14·9 *Enzymes and the metabolism of organic acids :* (B-12·8/68)

14·9·1 *: Bacterial degradation* (-) *citramalate :* Preliminary results using citramalate - C - 14 indicate that (-) citramalate is first activated to (-) citramalyl CoA and then degraded to pyruvate and acetyl-CoA. A new enzyme succinyl-CoA-(-) citramalate, CoA-transferase seems to be present in the active cell free extracts. Another enzyme citramalyl-CoA-lyase is also necessary for the formation of acetyl-CoA and pyruvate. Experiments are in progress to purify and study the specificity of these enzymes.

14·9·2 *: D* (+)*-Malate dehydrogenase :* This enzyme has been purifie about 25-30 fold. It seems to be similar to the D(+) -malic enzymes described in literature. However, it is optimally active only at pH 8·8 unlike the normal malic enzymes. Further purifications and studies on its properties are in progress.

15. PHYSICO CHEMICAL STUDIES ON POLYMERS

15·1 *Stereospecific polymerization :* (B-13·1/60)

In continuation of earlier studies on polymerization of methylmethacrylate with $VOCL_3$-$AlEt_3$ catalyst system, polymethylmethacrylate obtained was examined with NMR spectra. The stereoblock structure of the polymer has been attributed to the coordinate anionic mechanism.

In view of this finding, polymerization of methylmethacrylate was conducted in the presence of VCl_4-$AlEt_3$ catalyst system which is more stereospecific than $VOCl_3$-$AlEt_3$. In *n*-hexane medium, the catalyst system produced stereoblock structure in the polymer and the kinetic behaviour was in agreement with those of typical Ziegler-Natta catalysts. The same catalyst system was used for the polymerization of acrylonitrile and methylmethacrylate in the medium of basic compounds such as acetonitrile. Al/V ratios of 1 and 3 were effective for the polymerization of acrylonitrile and methylmethacrylate respectively. In both cases, the polymers obtained had linear structure and low molecular weight. In case of acrylonitrile, the initial rate of polymerization is independent of monomer concentration but decreases with catalyst concentration, whereas in the case of methylmethacrylate, it is proportional to both catalyst and monomer concentration. Kinetic behaviour showed different active sites and mechanism of reaction for acrylonitrile and methylmethacrylate. NMR studies showed the presence of heteroblock structure for the polymer which is characteristic of free radical mechanism. Further work is in progress to elucidate the mechanism of reaction by use of free radical inhibitors such as hydroquinones.

15·2 *Degradation of long chain molecules by ultrasonics :* (B-13·3/63)

The ultrasonic degradation of macromolecules has some resemblance to mechanical degradation i.e., mastication and the process is investigated on different industrially useful polymers. In conventional roller-pressed mastication of rubbers, the molecular weight of the end product is widely distributed, whereas in ultrasonic degradation, a relatively sharp molecular weight distribution is attained and that too, within a very short time with proper experimental conditions.

The kinetics of ultrasonic degradation of neoprene AD are being studied. As the higher molecular weight fractions when dried resulted in the formation of gel, the wet precipitate immediately after precipitation was dissolved with pure solvent and the resulting solution was made free from the last traces of non-solvent by distilling out the solvent/non-solvent azeotrope. The progress of degradation is being followed both by solution viscosity measurements as well as by estimation of free radicals as a function of DPPH consumed. The rate observed by estimation of DPPH is about twice faster than that obtained from solution viscosity data. In toluene solution, the degradation rate decreases with increase of solution viscosity.

16. CHEMICAL ENGINEERING STUDIES

16.1 *Design cell :* (AB-59/68)

The Design cell has completed the following items during the period under review :

(i) The complete process design for a semicommercial plant for chlorobenzenes of 300 tonnes per year capacity.

(ii) A chlorobenzene plant of 4500 tonnes per year capacity (80% monochlorobenzene).

(iii) Complete process design for a plant for 'Rubber reclaiming agent' of 100 tonnes per year.

16·2 *Fluidization :* (B-14·5/68)

A theoretical expression for the total optimization of a combined reactor (fluidized/fixed) has been derived. This optimization is with respect to mixing. The optimality criterion defined by this expression was verified by the results of the experiments carried out earlier on the catalytic vapour-phase oxidation of benzene. Since the reaction involved is complex and the criterion derived is essentially for a simple reaction, it was felt that a better way of verifying the criterion would be to carry out a simple reaction with negligible side products. Accordingly, the vapour-phase catalytic hydrogenation of nitrobenzene is being studied in a combined reactor.

Several experiments were carried out on the characteristics of a gas-liquid fluidized bed column with continuous flow of the liquid. These experiments were performed with gas, glass beads and sand, using air and water as the fluids. It is proposed to extend these studies to reacting system such as ammonia-water and examine the characteristics of such system based on the results obtained with non-reactive systems.

A fluidized bed column of 18" diameter has been set up with provision for different designs of column internals. The object of this study is to simulate tapered bed conditions in conventional cylindrical columns with appropriately designed internals. The entire reactor assembly is suspended on springs so that, by a suitable relay and recording of the vibrations, an index of bed uniformity can be formulated. This work will be useful to establish design criteria for scaling up fluid bed reactors to commercial size.

16·3 *Mass transfer* : (B-14·6/68)

Experimental and theoretical investigations were completed earlier on mass transfer during drop formation. A new model was proposed according to which the internal circulation in a forming drop is linked to the lines of force in a magnetic field. During the period under review, several systems were considered for extending this work to liquid-liquid reactive system during drop formation. A system which can conform to certain requirements has been chosen and experimental work will be commenced.

A model was proposed earlier for reaction between two gases in a liquid medium. It is proposed to extend this model to a system in which a suspended (dissolved) catalyst is involved. The system chosen is the reaction between hydrogen chloride and ethylene in a liquid medium.

Flooding and hold-up data in a pulsed column have been fitted to acceptable mathematical models. The flooding and hold-up data in conventional packed column have also been fitted to mathematical models which are simpler to use and which are more accurate than the reported equations.

16·4 *Diffusion in solid catalyst* : (B-14·7/68)

A theoretical expression has been derived for predicting the effectiveness factor of a catalyst in a nonisothermal system in the presence of adsorption. For this purpose, the effective diffusivity and the temperature profiles in a catalyst pellet have to be experimentally determined. A suitable experimental assembly in which the pellet can be prepared *in situ* has been assembled, together with an analytical apparatus involving the use of a conductivity cell. Experimental work is proposed to be commenced using the catalyst developed in this laboratory for aniline. The work will then be extended to the determination of effective diffusivity in zinc oxide which is one of the materials used in studies on gas-solid reacting systems.

16·5 *Reaction models and reactor design :* (B-14·8/68)

The complete kinetics of the dehydration of monohydric aliphatic alcohols has been worked out for C_2 to C_{10} alcohols. Reaction models have been proposed for each of these alcohols and it has also been possible to work out correlations for rate constants as well as adsorption constants. In correlating the rate constants, the difference in the entropy of formation of a given alcohol and that of a reference alcohol has been used as a correlating parameter, while in the case of adsorption constants the total binding energy of the alcohol involved has been used. Thus, a series of generalized correlations have been developed (for Indian bauxite as catalyst) which enable the determination of the kinetic parameters of any alcohol during its complex dehydration.

Theoretical equations have been worked out for predicting the transition from one regime of control to another in vapour-phase reactions catalysed by solids. This analysis also includes the effects of catalyst fouling and the possibility of a change in activation energy within a given regime.

An experimental assembly has been set up for studying the isomerization of 2-butene to isobutylene. In this work the experimental system has been so devised that adsorption and reaction on the catalyst can be simultaneously studied.

16·6 *Distillation :* (B-14·11/68)

A generalized correlation has been worked out for predicting the activity coefficient in a binary system. This correlation predicts the activity coefficient to within $\pm 10\%$ and can be advantageously used in the design of distillation columns.

16·7 *Development of a continuous process for the preparation of esters :* (AB-57/68)

Work was undertaken to produce esters like DBP by a continuous process, instead of the batch process developed earlier. Equipment was designed, set-up and a few preliminary runs were carried out. Conversion was low in these runs, however, by proper choice of the variables such as feed rate, temperature, residence time etc., good conversions would be possible. Work is being continued along with other work on phthalates.

16·8 *Heat transfer :* (B-14·2/66)

Experimental work to study the performance of packed column for direct contact heat transfer between water and oil was completed. The data collected are being analysed.

□ □ □

APPENDICES

A-I SERVICE PROJECTS

1. *Physico analytical work*

Analytical and quality control work was conducted for the various projects in progress in the laboratory.

2. *Microanalysis*

Microanalysis of organic compounds for various elements (C, H, N, halogen, sulphur), functional groups (methoxyl, acyl, C-methyl, N-methyl, active hydrogen), molecular weight etc., was carried out.

1975 analyses for elements and 33 for functional groups were carried out.

3. *Spectrochemical work*

Analytical and structure elucidation work was carried out by various physico organic techniques such as UV, IR, NMR, visible spectra and mass spectra.

Number of samples studied :

NMR	...	2561
UV	...	623
UV visible	...	513
IR	...	4324
Mass spectra	...	898

4. *VPC/GLC analysis*

6493 samples were analysed.

5. *X-ray patterns*

60 X-ray powder patterns were obtained.

6. *Ultracentrifugal analysis*

110 samples were analysed.

7. *Instrumentation*

Servicing and maintenence of the following special equipments were carried out: NMR spectrometer; IR, UV and visible spectrophotometers; X-ray machine; electrical furnances; gas chromatographs; colorimeters; servo-recorders, etc.

Running and maintenance of the liquid air plant and supply of liquid air to various groups in NCL was attended to.

Total number of jobs completed : 328

8. *Workshop*

Special equipment fabricated :

	Item	Nos.
(i)	Electron diffraction camera	2
(ii)	A pilot plant unit for chlorobenzene project	1
(iii)	Butadiene condensing unit	1
(iv)	M. S. lead lined reactor with M. S. stand. (Reactor size 10"×5")	1
(v)	M. S. autoclave 5" dia × 7½" ht. to stand 250 psi. pressure.	1
(vi)	M. S. reactor for methyl chlorosilane project.	1

Total number of jobs completed : 2764.

9. *Glass blowing*

Jobs completed : 4700

5400 standard ground glass joints were fabricated.

10. *Technical services*

The economics of the following NCL processes was evaluated and proposals for the terms and conditions of their release were put before the Process Release Committee for approval: rubber blowing agent, coating for oil filter paper, sealants for canvas bags, rubberized cork sheets, dibutyl and dioctyl phthalates, stabilized gel for making hot and cold sachets, ferric oxide, chlorobenzene, aniline, butyl titanate, optical whitening agent, *p*-tert-butyl catechol, recovery of pyridine bases from their aqueous solutions, cadmium sulphide photo cells.

To arrive at more realistic cost estimates, revised norms for cost calculations were framed for the approval of the Process Release Committee. Economic evaluation and cost estimates were prepared for the following processes: cetostearyl ethylene oxide condensation product used as evaporation retardant, styrenated alkyds, exaltolide, mixed NP-fertilizers.

Fresh terms and conditions for sponsored research were drafted for the approval of the Process Release Committee. Proposals for sponsoring the various projects were prepared and sent to the prospective entrepreneurs.

The project on chlorobenzene was programmed by the application of of PERT (Programme Evaluation Review Technique).

Commercial intelligence : Market surveys of *p*-toluene sulphonamide and polyurethane coatings were carried out.

Data regarding the availability, prices etc., on chemical raw materials was collected.

Industrial liaison : As a follow-up, information on the performance of the NCL processes released to various parties and their experience on the know-how supplied was collected.

A large number of technical enquiries from different industries, Parliament and Government organisations were attended to. In addition, comments were offered on new licence applications and agreement for the release of NCL know-how were processed.

In connection with CSIR silver jubilee celebrations, 'Open Day' exhibition was organized at the Laboratory on 10th and 11th August, 1968. More than 15000 people visited the above exhibition. In addition, 2356 visitors were taken round the Laboratory during the year.

Research management : The Division has undertaken active study on various aspects of research management. Some of the major aspects covered were: transfer of technology, patent system, foreign collaboration, NCL projects case studies, contractual research.

The following surveys were conducted: patent system in various countries, survey on NCL Annual Reports 1948-64, patent survey (1951-68) on dyes and intermediates.

Publications : The following publications were brought out: annual report (1967-68), NCL brochure.

Internal reports : Performance of NCL during the I/II five-year plan, NCL pilot plants, norms of input calculations for 1969-70 and proposals for the IV five-year plan, half yearly report (April-September 1968), research programme (1969-70).

In addition to the above, a few features on NCL and its processes were sent to various journals and dailies for publication.

General service : The Division continued to render statistical, photographic, museological and draftsman services to other divisions of the Laboratory.

A-II. SERVICES RENDERED TO OUTSIDE PARTIES

1. *Supply of cultures*

612 cultures from NCIM were supplied free of charge to various institutions in India and abroad.

2. *Analytical services*

	No. of analyses	Charges received (Rs.)
Microanalysis	77	1,074
GLC analysis	18	800
VPC analysis	2	100
NMR	31	980
UV	4	160
IR	31	345
Mass spectral analysis	184	13,800
X-ray powder pattern	8	160
Surface area measurements	13	650
Water analysis	44	1,100
Total	412	19,169

3. *Technical aid involving ad-hoc experimental, instrumental, engineering and glass blowing services :*

1.	Repairs of Beckman pH meter, photovolt electronic pH meter, hand refractometer, Gallenkamp soil tensometer, irrometer, soil moisture indicator.	Agricultural Department, Government of Maharashtra, Padegaon.
2.	Repairs of Beckman zerometric pH meter.	CPHERI Field Station, Poona.

3. Following glass-blowing work was carried out.

(*a*)	Fabrication of calomel electrode and glass apparatus, (as per sketch), gas Lasers apparatus and repairs of mercury distillation glass equipment.	Institute of Armament Technology, Girinagar, Poona, (Charges: Rs. 265).
(*b*)	Fabrication of sintered glass funnel filter.	Small Industries Res. Institute, Poona, (Charges Rs. 190).
(*c*)	Fabrication of traps, thermonell, claisen head mercury seal, magnetic stirring needle, vacuum distillation unit, and stirring rods.	Space Science & Technology Centre, Trivandrum, (Charges Rs. 250).
(*d*)	Fabrication of all glass high vacuum evaporation unit with McLeod gauge, mercury diffusion pump and liquid trap.	Shivaji University, Kolhapur. (Charges Rs. 1,000).
(*e*)	Fabrication of one fractionating column.	Medical Plants Scheme, Chinchona Deptt. Ootacamund, (Charges Rs. 1,200).
(*f*)	Fabrication of 'H' type calomel electrode.	Department of Agriculture, Poona, (Charges. Rs. 100).
(*g*)	Fabrication of Tucker's carbon dioxide generator Schoniger flask, micro-filter tubes.	Indian Dyestuffs Industries, Kalyan, (Charges Rs. 2,000).
(*h*)	Fabrication of spinning band column.	Indian Institute of Science, Bangalore, (Charges Rs. 50).
(*i*)	Repairs of condensers of Buchi model, rotary evaporator.	Karnatak University, Dharwar, (Charges Rs. 75).

(*j*)	Fabrication of 3 necked—20 lt. round bottom flask.	Coated Fabrics (P) Ltd., Lonavala, (Charges Rs. 100).
(*k*)	Repairs of 3 necked—20 lt. round bottom flask.	Super Products Manufacturing Co., (P) Ltd., Poona, (Charges Rs. 35).
(*l*)	Repairs of quick fit and pyrex glassware.	Hindustan Antibiotics Ltd., Pimpri, (Charges Rs. 500).
(*m*)	Repairs of glass articles	Central Water & Power Research Station, Poona, (Charges Rs. 75).
4.	Grease-proof paper analysed quantitatively and qualitatively.	M/s Pudumji Pulp & Paper Ltd., Poona, (Charges Rs. 300).
5.	Copper strips analysed, quantitatively.	M/s Diamond Clock Manufacturing Co. (P) Ltd., Poona, (Charges Rs. 100).
6.	Aluminium silicate samples (3 nos.) analysed.	M/s Swastik Rubber Products Ltd., Kirkee, Poona, (Charges Rs. 600).
7.	Standardization of 5-hydroxytryptamine estimations in plasma and platelets.	Department of Physiology, Armed Forces Medical College, Poona.

Total receipts : Rs. 6,840

A-III DEMONSTRATIONS

Following processes were demonstrated :

Rubber reclaiming agent	M/s Swastik Rubber Products Ltd., Kirkee, Poona.
Rubber blowing agent	— do —
Resins for automobile filters	M/s White Cloud Paper Mills, Poona.

A-IV PROCESSES LEASED OUT DURING 1968-69

Process	*Party*	*Remarks*
1. β-Ionone	M/s Industrial Perfumes Ltd., Bombay.	Non-exclusive
2. Dithranol	M/s Indian Dyestuffs Industries Ltd., Bombay.	Exclusive (NRDC agreement in progress).
3. Cadmium sulphide photo-conductive cells	M/s Gera Engineering Co., Poona-1.	Non-exclusive (NRDC agreement in progress)
4. Coating for oil filter paper	M/s White Cloud Paper Mills, Poona.	Technical aid, Non-exclusive.
5. Phthalates—dioctyl and dibutyl	M/s Alta Laboratories, Ltd., Bombay	Non-exclusive.
6. Rubber blowing agent	M/s Swastik Rubber Products Ltd., Poona.	Technical aid, Non-exclusive.
7. Rubber reclaiming agent	—do—	Non-exclusive. (NRDC agreement in progress.)
8. Vapour phase chromatograph	M/s Associated Instruments Manufacturers India (P) Ltd., New Delhi.	Exclusive.
9. Hard ferrites	M/s Semiconductors (P) Ltd., Poona.	Non-exclusive.

A-V SPONSORED PROJECTS COMPLETED DURING 1968-69

1. Utilization of longifolene	M/s Camphor & Allied Products Ltd., Bareilly.
2. Utilization of Δ^3-carene	— do —
3. Utilization of terpene-G	— do —
4. BD-catalyst	M/s Synthetics & Chemicals Ltd., Bombay.
5. Tung oil (PL-480)	U. S. Department of Agriculture, Washington, D. C.

6.	Titanium tetrachloride from ilmenite	M/s Travancore Titanium Products Ltd., Trivandrum.
7.	Water evaporation control (PL-480)	U.S. Department of Agriculture, Washington, D. C.
8.	Radio opaque dyes	M/s Unichem Laboratories, Bombay.
9.	Sorbide nitrate	M/s Indian Schering Ltd., Bombay.
10.	Anthraquinonoid dyes	M/s Indian Dyestuffs Industries Ltd., Bombay.
11.	Steroids and wax from sugarcane press mud	M/s Brihan Maharashtra Sugar Syndicate Ltd., Poona.
12.	Development of adhesives for decorative laminates	M/s Swastik Rubber Products Ltd., Poona.
13.	Lac dye	Indian Lac Cess Committee, Ranchi.
14.	Industrial chemicals from diketene	M/s Aniline Dyestuffs & Pharmaceuticals Ltd., Bombay.
15.	Perfumery grade geraniol, citronellal and citronellol	M/s Radhakishan Rajaram & Co., Bombay.

A-V (1) RECEIPTS THROUGH SPONSORED PROJECTS

		Rs. in lakhs
(i)	Total receipts from above completed sponsored projects	2·48
(ii)	Total receipts from other sponsored projects during the year 1968-69 which are being continued in 1969-70	3·74
(iii)	Total receipts from sponsored projects during 1968-69	6·22

A-VI TRAINING

Ten scientists from different universities, industries and research institutes were trained in one of the following :

Electron diffraction techniques; surface area measurements by the BET technique; use of the polarograph; physico analytical techniques; thermal degradation of low-density polyethylene; ultra-centrifuge techniques, etc.

Students from National Talent Scheme and other post graduate students from colleges and universities were given training during vacation.

A-II SEMINARS AND LECTURES

Weekly seminars are held at NCL in which members of the scientific staff take an active interest. In addition to the talks by several NCL scientists, the following lectures were delivered by outside eminent scientists at NCL :

Dr. C. C. Patel, Indian Institute of Science, Bangalore-12.	Some complex compounds of neutral monodentate ligands.
Prof. J. Th. Hackman, Technical University, Trente, Holland.	The influence of matter on the mind.
Dr. Miss Margaret K. Seikel, CSIRO, Division of Forest Products, South Melbourne, Australia.	(i) New Lignans of ulmustomasii (Roek clm) heartwood.
	(ii) Phenolics of *Querens rubra* (northern red oak) sapwood and heartwood in connection with problems of discolouration.
Prof. H. Zollinger, Swiss Federal Institute of Technology, Zurich.	Metastable intermediates in electrophilic aromatic substitution.
Prof. R. M. Acheson, Queens College, Oxford, U. K.	Addition to heterocyclic compounds and other related topics (3 lectures).
Prof. P. T. Narsimhan, IIT, Kanpur.	(i) Electron spin resonance study of the structure of free radicals solution.
	(ii) Extended Huckel study of shapes of molecules in the ground state and the transition state.
Prof. H. C. Brown, Purdue University, U.S.A.	The versatile organoboranes.

Dr. A. N. Malaviya, Allahabad University, Allahabad.	Electron transport in submito chondrial systems.
Prof. T. J. Bardos, State University of New York, U. S. A.	Chemical and biochemical studies with 5-substituted pyrimidine nucleosides.
Prof. T. Urbanski, Department of Technical Politechnika, Poland.	(i) Heterocylic compounds. (ii) Synthesis of new drugs.
Dr. D.S. Ambwani, Case Western Reserve University, Cleveland, Ohio, U.S.A.	Absorption of mercury-cyclohexane interphase.
Dr. R. E. Hester, University of York, Hestington, U. K.	Vibrational spectroscopy of molten salts.
Prof. L. Farkas, Technical University, Budapest, Hungary.	Benzal chromanones and camaranones.
Prof. H. L. Strauss, University of California, Berkeley, U.S.A.	Configuration of small ring molecules as studied by Far Infra-red spectroscopy.
Dr. R. J. Ferrier, Birbeck College, London, U. K.	Physical methods in carbohydrate chemistry.
Dr. D. B. Anderson, School of Polymer Science, University of Bradford, Bradford, U. K.	Rubber modified thermoplastics.
Prof. G. E. Kricheveskу, Moscow Textile Institute, Moscow, U.S.S.R.	(i) Interaction of reactive dyes with cellulosic fibres. (ii) Interaction of reactive dyes with protein and polyamide fibres. (iii) Stability of bond between reactive dye and fibre substance to different agencies.

Nine NCL scientists delivered more than 15 scientific lectures on different subjects at various institutes and universities in the country.

1. *Foreign deputations/training etc.*

Dr. B. D. Tilak attended the third meeting of the Indo-U.A.R. Joint Scientific Board in Cairo as a member of the Indian delegation (April/May 1968).

Mr. P. H. Brahme returned from U.S.S.R., after receiving training in 'Problems in high pressure polymerization' under the auspices of Indo-Soviet Cultural Exchange Programme, 1967-68 (October 1968).

Mr. V. Krishnan proceeded to East Germany for training in 'Process development and reaction kinetics: pilot plant design and operation, evaluation of data etc.' under the plan for cooperation between the German Academy of Sciences and the C.S.I.R., (June 1968).

Dr. Sukh Dev attended Indo-Soviet Joint Symposium on 'The chemistry of natural products' at Tashkent, U.S.S.R., as a member of Indian delegation (September 1968).

Dr. J. Gupta visited Yugoslavia as a member of Indian delegation. He discussed the programme of scientific cooperation between India and Yugoslavia under a bi-lateral agreement. He also acquainted himself with some of the scientific institutions in Yugoslavia (October 1968).

Dr. V. S. Pansare proceeded to Czekoslovakia to receive training in 'The field of instrumental analytical chemistry and modern methods of separation' under the Exchange Programme between the C.S.I.R. and Czekoslovakia Academy of Sciences, (January 1969).

2. *Awards and honours*

Dr. J. L. Bose and Dr. N. L. Dutta were awarded 'Silver Jubilee Service Awards' during the celebrations of the C.S.I.R., Silver Jubilee (August 1968).

Dr. B. V. Ramachandran was awarded D. Sc. by Madras University.

3. *Ph. D. degrees received by NCL staff and research fellows*

Name	*University*
Arora, S. K.	Poona
Audichya, T. D.	Poona
Ballal, N. R.	Poona
Bhadane, N. R.	Poona

Bhagwanth, M. R. R.	Bombay
Bindra, A. A.	Poona
Chavan, A. M.	Poona
Dixit, S. M.	Bombay
Hiremath, S. V.	Poona
Iyer, V. N.	Bombay
Jindal, S. L.	Bombay
Joshi (Miss), M. D.	Poona
Krishnappa, S.	Poona
Madhyastha, K. M.	Poona
Manjrekar, T. G.	Bombay
Nerali, S. B.	Poona
**Pandit, S. K.	Bombay
* Pathak, S.	Bombay
Panse, G. T.	Bombay
Phadke, V. B.	Poona
Reddy, A. K.	Bombay
Sarma, M. R.	Poona
Subbaswami, K. N.	Bombay
Umapathy, P.	Poona
Umrani, D. C.	Poona
Upadhya, A. B.	Poona
Welenkiwar, S. S.	Poona

* Awarded M.Sc.

** Awarded M.Sc. (Tech.)

4. *NCL scientists recognized by different universities as research guides*

Dr. Bose, J. L.	Bombay, Poona, Nagpur, Shivaji.
Dr. Chakravarti, K. K.	Bombay, Poona, Shivaji.
Dr. Dadape, V. V.	Bombay, Poona, Karnatak, Vikram, Banaras.
Dr. Damodaran, V.	Shri Venkateswara University, Tirupathi.
Dr. Das, K. G.	Poona, Bombay, Kerala.
Dr. Doraiswamy, L. K.	Poona, Bombay, Nagpur, Calcutta, Jadavpur.
Dr. Dutta, N. L.	Poona.
Dr. Ghatge, B. B.	Poona.
Dr. Ghatge, N. D.	Poona, Bombay, Shivaji.
Dr. Gogte, V. N.	Shivaji.

Dr. Goswami, A.	Calcutta, Poona, Punjab.
Dr. Gupta, J.	Bombay, Poona, Punjab, Madras.
Dr. Iyyangar, N. R.	Poona.
Dr. Jagannathan, V.	Bombay, Poona.
Dr. Kapur, S. L.	Bombay, Poona, Punjab.
Dr. Katti, S. S.	Bombay.
Dr. Kelkar, G. R.	Poona.
Dr. Kulkarni (Miss), S. B.	Poona.
Dr. Kulkarni, S. N.	Poona, Bombay, Karnatak, Shivaji.
Dr. Mathur, H. B.	Poona, Agra, Madras, Bombay, I.I.T., Bombay.
Dr. Nair, P. M.	Poona, Shivaji, Andhra.
Dr. Narayanan, C. R.	Poona, Bombay, A. B. University.—Zaria, (Nigeria).
Dr. Pai, M. U.	Bombay.
Dr. Pant, L. M.	Poona.
Dr. Rangachari, P. N.	Poona.
Dr. Rao, A. S.	Poona, Bombay, Shivaji.
Dr. Rao, M.R.R.	Bombay, Poona.
Dr. Sadana, J. C.	Poona, Aligarh.
Dr. Sen, D. N.	Poona, Bombay.
Dr. Sinha, A. P. B.	Poona, Banaras, Vikram, Karnatak.
Dr. Sivaraman, C.	Poona.
Dr. Subbaraman, P. R.	Poona, Bombay, Gujarat, Kerala.
Dr. Sukh Dev	Poona, Bombay, Agra, Punjab, I.I. Sc., Bangalore.
Dr. Tilak, B. D.	Bombay, Poona.
Dr. Venkataraman, K.	Poona, Bombay, Madras, Banaras.

5. *NCL scientists working as consultants*

Dr. Tilak, B. D.	(i) M/s. Aniline Dyestuffs and Pharmaceuticals P.Ltd., Bombay. (ii) M/s. Surfactants P. Ltd., Bombay. (iii) M/s. Amar Dye Chem. Ltd. Kalyan.

Dr. Mitra, R. B.	M/s. Alta Laboratories, Ltd., Khopoli.
Dr. Chakravarti, K. K.	M/s. Sunanda Aromatic Industries, Mysore.
Dr. Kapur, S. L.	M/s. J. K. Synthetics Ltd., Kanpur.

A-IX PUBLICATONS

Research papers :

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MÖssbauer spectra of oxidic spinels containing Sn$^+$ ion.
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2. Yagnik, C. M. and Mathur, H. B.
A MÖssbauer and X-ray diffraction study on the cation distribution in FeAl$_2$O$_4$.
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3. Yagnik, C. M. and Mathur, H. B.
Charge distribution in the mixed oxide systems-ZnMn$_x$Fe$_{2-x}$O$_4$ and CoMn$_x$Fe$_{2-x}$O.
Indian J. Pure Appl. Phys. **6**, 211 (1968).

4. Pethe, L. D., Mathur, H. B. and Biswas, A. B.
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5. Badrinarayanan, S. and Mathur, H. B.
Impurity diffusion of antimony and silver in aluminium.
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9. Katti, S. S., Natekar (Miss), M. V. and Pathak, Samir.
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Chemical effects of electron capture in ^{57}Co (III) (1-10 phenathroline)$_3$ $(ClO_4)_3.2H_2O$.
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Indian J. Chem. **7**, 28 (1969).

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Synthesis of benzo(c) thiphene and naphtho(c) thiphene.
Indian J. Chem. **7**, 9 (1969).

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60. Narayanan, C. R. and Iyer, K. N.
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Indian J. Chem. 5, 218 (1967).

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Bhattacharyya, S. C.
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90. Siscovic (Mrs.), E., Chaudhari, P. N. and Rao, A. S.
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Chem. Engg. Science **23**, 537 (1968).

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2. Das, K. G., Nayar, M. S. B. and Joshi, B. S.
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University College, London, September 1968.

3. Narayanan, C. R.
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5. Ranjekar (Miss), V. K. and Jagannathan, V.
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   Chemical Age of India **19,** 1105 (1969).

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1. **54867**
   A process for the manufacture of nicotine sulphate from tobacco and tobacco wastes.
   Bijawat, H. C., Razdan, R. and Potnis, G. V.

2. **56726**
   Preparation of water dispersible DDT as an oil bound paste.
   Rao, K. V. N., Bhide, S. P., Kulkarni (Miss), S. B. and Biswas, A. B.

3. **57888**
   Improvements in or relating to the production of hydroxy, alkoxy or aryloxy substituted aryl alkyl ketones.
   Bose, J. L. and Shah, R. C.

4. **58868**
   A process for the preparation of azelaic acid semiester suitable for making civetone dicarboxylic acid.
   Nayak, U. G., Chakravarti, K. K. and Bhattacharyya, S. C.

5. **59419**
   A process for the preparation of tridecane 1 : 13 dicarboxylic acid or its ester, suitable for the preparation of exaltone (cyclopentadecanone).
   Ghatge, B. B., Nayak, U. G., Chakravarti, K. K. and Bhattacharyya, S. C.

6. **59497**
   Production of porous polymer suitable for preparing cation exchange resins.
   Govindan, K. P., Pandya, R. N. and Krishnaswamy, N.

7. **59606**
   Preparation of cation exchange resin from porous cashewnut shell liquid polymer.
   Krishnaswamy, N., Pandya, R. N. and Govindan, K. P.

8. **59608**
   Rigid filters.
   Kapur, S. L. and Pandya, R. N.

9. **59853**
Improvements in or relating to the preparation of costus root oil and the isolation of lactonic constituents therefrom.
Kelkar, G. R. and Bhattacharyya, S. C.

10. **60555**
Production of liquid rubber.
Uma Shankar

11. **60826**
Improvements in or relating to the production of hydroxy, alkoxy or aryloxy substituted deoxybenzoins and particularly of deoxyanisoin.
Bose, J. L. and Shah, R. C.

12. **62890**
A new process for the production of 4-hydroxycoumarin and its derivatives.
Shah, V. R., Bose, J. L. and Shah, R. C.

13. **63083**
A new method for the preparation of 4-hydroxycoumarins.
Shah, V. R., Bose, J. L. and Shah, R. C.

14. **64958**
Improvements in or relating to polishing compositions.
Shah, S. M., Hinge, V. K., Mhaskar, V. V. and Shah, R. C.

15. **65440**
A process for the extraction of wax from sisal waste.
Shah, S. M., Hinge, V. K., Mhaskar, V. V. and Shah, R. C.

16. **65543**
A process for the preparation of ω-dicarboxylic acids and ω-hydroxy acids suitable for conversion to macrocyclic compounds.
Mathur, H. H. and Bhattacharyya, S. C.

17. **65778**
Improvements in or relating to the production of transdiethylstilbestrol dimethyl ether and allied stilbenes.
Joshi, C. G., Bose, J. L. and Shah, R. C.

18. **65976**
Improvements in or relating to suspension polymerization of vinyl monomers.
Joshi, R. M. and Kapur, S. L.

19. **65977**
Rubber-base adhesive.
Uma Shankar.

20. **66096**
A process for the production of bacterial diastase by submerged culture.
Babbar, I. J., Bekhi, R. M. and Srinivasan, M. C.

21. **66194**
Improvements in or relating to can sealing composition.
Raghunath, D. and Kapur, S. L.

22. **66803**
Improvements in or relating to the manufacture of pressure sensitive adhesive tapes.
Kapur, S. L. and Rao, B. R. K.

23. **66836**
Manufacture of ethylene dichloride.
Banerjee, S. C., Pathak, S. L., Pai, M. U. and Doraiswamy, L. K.

24. **66966**
An improved process for the manufacture of porous rigid filters.
Kapur, S. L. and Pandya, R. N..

25. **67490**
Improvements in or relating to the preparation of adhesive tape.
Kapur, S. L. and Rao, B. R. K.

26. **67513**
Improvements in or relating to the separation of niobium and tantalum from each other by liquid-liquid extraction.
Sarma, B. and Gupta, J.

27. **70670**
Improvements in or relating to the controlling of water evaporation for conserving water in lakes and reservoirs.
Kulkarni (Miss), S. B., Gharpurey, M. K., Deo, A. V., Sanjana, N.R., Abraham, K. O. and Subba Rao, B. C.

28. **71063**
Production of bacterial protease by submerged culture.
Babbar, I. J., Powar, V. K. and Janannagathan, V.

29. **71190**
Preparation of anion exchange resins.
Krishnaswamy, N., Govindan, K. P., and Dasare, B. D.

30. **72425**
A direct process for preparing the chlorides of barium and strontium from their sulphate minerals.
Iqbal, S. H., Lobo, J. and Gupta, J.

31. **73702**
A process for the preparation of cyclopentadecanolide (exaltolide).
Dhekne, V. V., Ghatge, B. B. and Bhattacharyya. S. C.

32. **74356**
Preparation of insoluble reaction products of polystyrene for use as cation exchange materials.
Govindan, K. P. and Krishnaswamy, N.

33. **74451**
Preparation of covering materials from anacardic materials.
Raghunath, D., Suryanarayana, N. P. and Krishnaswamy, N.

34. **77080**
A process for the preparation of ambrettolide.
Sabnis, S. D., Mathur, H. H. and Bhattacharyya, S. C.

35. **77081**
Improvements in or relating to the preparation of polyamide compounds and their compositions as antipriming agents in steam generators.
Pathak, K. D. and Subba Rao, B. C.

36. **77225**
A process for the preparation of β-ionone from pseudoionone.
Joshi, B. N., Chakravarti, K. K., Shah, R. C. and Bhattacharyya, S. C.

37. **82189**
Production of dextro-tartaric and oxalic acids.
Vartak, H. G., Patil, S. G. and Jagannathan, V.

38. **82822**
A process for the manufacture of high alpha cellulose dissolving grade pulps by alkaline pulping methods.
Vyas, G. M., Bendale, D. S. and Mahajan, M. B.

39. **83364**
Manufacture of hexachloroethane.
Bhat, N. A., Goswami, M. and Pai, M. U.

40. **83716**
Manufacture of nicotine sulphate from tobacco wastes.
Potnis, G. V., Goswami M., Ramachandran, V. and Pai, M.U.

41. **86541**
A reactor for carrying out highly exothermic and explosive reactions particularly suited for chlorination of methane.
Mukherjee, S. P., Deshpande, A. D., Potnis, G. V. and Pai, M.U.

42. **86638**
A process for the preparation of 2-iso-propenylhexanols.
Ramaswami (Mrs.), S., Ramaswami, S. K. and Bhattacharyya, S. C.

43. **86991**
Preparation of polyurethane printing rollers.
Ghatge, N. D. and Kapur, S. L.

44. **90574**
A process for the preparation of *dl*-muscone.
Nair, M. S. R., Mathur, H. H. and Bhattacharyya, S. C.

45. **91412**
Manufacture of 2, 3-hydroxynaphthoic acid from 2-naphthol.
Phadtare P. G., Srinivasan, K. R., Baliga, B. A., Kotasthane, M. G. and Doraiswamy, L. K.

46. **92977**
Improvements in or relating to the manufacture of hexachloroethane.
Mukherjee, S. P., Goswami, M., Soundararajan, S., Sadasivan, N., Sen, R. K. and Doraiswamy, L. K.

47. **96663**
A new process for the manufacture of glycolic acid.
Vartak, H. G. and Patil, S. G.

48. **98156**
Preparation of solvent modified copolymers of vinyl monomers in bead form.
Kapur, S. L. and Ramkrishanan, K.

49. **96801**
A new method for the improvements in the figure of merit of thermoelectric material.
Narasimhan, K. S. V. L. and Sinha, K. P.

50. **98155**
An improved method for the hydration of sulphonated mixtures of vinyl copolymer beads containing 90-95% sulphuric acid and the sulphonated vinyl copolymer beads.
Kapur, S. L. and Ramakrishnan, K.

51. **99590**
Process for the manufacture of a novel binding agent for core sand.
Varma, J. P.

52. **101161**
Process for the preparation of day light and pink light emitting electro-luminescent phosphors.
Ambardekar, D. S. and Biswas, A. B.

53. **106804**
Improvements related to the manufacture of carboxy methyl cellulose.
Bendale, D. S., Mahajan, M. B. and Khadilkar, H. P.

Patents filed :

1. **81071**
Improvements in or relating to the recovery of nickel and fat from spent nickel hydrogenation catalyst.
Murthy, M. N. S. and Biswas, A. B.

2. **81072**
Improvements in or relating to the preparation and production of catalysts for the hydrogenation of organic substances with particular reference to fatty oils.
Murthy, M. N. S. and Biswas, A. B.

3. **94766**
Improvements in or relating to the preparation of jatamansi root oil and isolation of a coumarin constituent therefrom.
Unni, I. R., Maheshwari, M. L., Paknikar, S. K. and Bhattacharya, S. C.

4. **106808**
Improvements in or relating to the preparation of mixed oxide ceramic compositions.
Murthy, M. N. S. and Sinha, A. P. B.

5. **108413**
A process for treatment of costus roots (*Saussurea lappa Clarke*) for isolation of inulin.
Kulkarni, G. H., Kelkar, G. R., Bose, J. L. and Bhattacharyya, S. C.

6. **108414**
A process for treatment of costus roots for inulin isolated therefrom for the production of fructose.
Kulkarni, G. H., Kelkar, G. R., Bose, J. L. and Bhattacharyya, S. C.

7. **109489**
Production of aryl-glycosides.
Ingle, T. R. and Bose, J. L.

8. **111311**
A process for the recovery of anhydrous pyridine bases from their aqueous solution.
Buzruk, N. K., Paul, R. N., Potnis, G. V. and Pai, M. U.

9. **112575**
Thermal treatment of oil with catalyst.
Sukh Dev and Nayak, U. R.

10. **113406**
A new thermistor composition exhibiting high positive temperature coefficient of resistivity (Posistor).
Brahmecha, B. G. and Sinha, K. P.

11. **113703**
Improvements in or relating to magnesium zinc ferrites.
Krishan Rao, V. V., Kanade (Miss), S. B. and Sinha, A. P. B.

12. **113825**
11 ORT nickel zinc ferrites.
Krishna Rao, V. V., Kanade (Miss), S. B. and Sinha, A. P. B.

13. **116453**
Disperse dyes for polyesters with good affinity and sublimation fastness.
Raman, S. K. and Tilak, B. D.

14. **116675**
A process for the preparation of polyamide polymers using diisocyanates.
Ghatge, N. D., Patil, S. B. and Patil, V. S.

15. **117210**
A direct process for the manufacture of dibutylin di-iodide and of the oxide therefrom.
Gupta, J., Gopinathan, C., Gopinathan (Mrs.), S. and Awasarkar, P. A.

16. **117403**
Preparation of water thinnable emulsion paints from linseed oil.
Kapur, S. L. and Bakshi, S. H.

17. **118476**
Methods of preparing isocyanates, mono and polyureas from pentadecenyl phenol (Anacardol) and their uses.
Ghatge, N. D. and Yadav, S. D.

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A-XI TABLE I : PRODUCTS MANUFACTURED ON THE BASIS OF NCL KNOW-HOW

S. No.	Name of the process & Indian Patent Number	Field of utilisation	Name of the manufacturer (year of commencement of production)	Production — Qty. & value 1968-69	Upto Mar. 68	Remarks
1	2	3	4	5	6	7
1.	Acriflavine (sponsored)	Pharmaceuticals	Western India Fine Chemicals, C/o. M/s Bhaidas Karsandas & Co., 16, Apollo Street, Bombay-1 (1968).	—	—	Exclusive. Regular commercial production started. According to the party, they are producing by a different process.
2.	Anion exchange resin from melamine (71190)	Demineralization of liquids	M/s Tulsi Industries, Hadapsar Industrial Estate, Poona-13 (1963).	15 cft. Rs. 5,250/-	550 cft. Rs. 1,70,000/-	Non-exclusive.
3.	Antipriming compositions (77081)	Antipriming in locomotives	Research, Design and Standard Organization, M & C Wing, Chittaranjan (1964).	15,400 kg. Rs. 35,450/-	59,300 kg. Rs. 1,21,500/-	Non-exclusive.
4.	Bacterial diastase (66096)	Textile desizing	M/s Chemaux Pvt. Ltd., Mahim, Bombay-16 (1959)	850 kg. Rs. 85,500/-	—	Exclusive. Trial production Installed capacity 750 kg./month.

1	2	3	4	5	6	7
5.	Benzoic acid (sponsored)	Pharmaceuticals	M/s Aniline Dyestuffs & Pharmaceuticals (P) Ltd., 28, Apollo Street, Bombay-1 (1969).	Worth Rs. 17,000/-	—	Exclusive. Trial production started.
6.	Berberine hydrochloride (sponsored)	Pharmaceuticals	M/s G. Vallabhdas & Co., 180/82, Samuel Street, Bombay-9 (1965).	Information awaited.	300 kg. Rs. 36,000/-	Exclusive.
7.	Calcium hypophosphite (sponsored)	Pharmaceuticals	M/s Chunilal Ootamchand & Co., 79-F, Princess Street, Bombay-2 (1967).	3,000 kg. Rs. 1,70,000/-	250 kg. Rs. 10,000/-	Exclusive.
8.	Calcium silicate (sponsored)	Low density insulators	M/s Newkem Products Corp., Harganga Mahal, Bombay-14 (1968).	112 tonnes Rs. 3,90,000/-	—	Exclusive. Production capaticty 2T/day.
9.	Can sealing composition (66194)	Metal can industry	M/s Arya Chemical Works, 114/2A, Dharamtolla Street, Calcutta-13 (1962).	18,200 kg. Rs. 91,300/-	94,000 kg. Rs. 4,94,000/-	Exclusive.
10.	Cation exchange resin from CNSL (59497, 59606)	Demineralization of liquids	M/s Tulsi Industries, Poona-13 (1960).	110 cft. Rs. 12,100/-	7,200 cft. Rs. 6,01,500/-	Exclusive.
11.	Chloral hydrate (sponsored)	Industrial chemicals	M/s Hindustan Insecticides Ltd., Industrial Area, New Delhi-15 (1963).	2,900 kg. Rs. 37,800/-	12,000 kg. Rs. 1,04,000/-	Exclusive.

1	2	3		4	5	6	7
12.	Coating for oil filter papers	Oil filtration		M/s White Cloud Paper Mills, 412, Gultekdi Road, Poona-9 (1968).	—	—	Non-exclusive. Technical aid. Trial production started.
13.	DDT-water dispersible (56726)	Insecticides	(i)	M/s South India Research Institute (P.) Ltd., Sirinagar Industrial Estate, Vijayawada-7 (1963).	640 kg. Rs. 4,400/-	19,200 kg. Rs. 1,30,400/-	Non-exclusive.
			(ii)	M/s Lotus Industries, 62/20, Luz Church Road, Madras-4 (1967).	400 kg. Rs. 3,000/-	70 kg. Rs. 500/-	Non-exclusive.
14.	Dihydroisojasmone	Perfumery		M/s S. H. Kelkar & Co. (P.) Ltd., Bombay-Agra Road, Bombay-80 (1965).	300 kg. Rs. 1,02,000/-	40 kg. Rs. 12,000/-	Non-exclusive. Technical aid.
15.	Ethylene oxide condensates (sponsored)	Surface active agent		M/s Hico Products (P.) Ltd. Mogal Lane, Bombay-16 (1965).	2,86,900 kg. Rs. 35,25,600/-	4,01,800 kg. Rs. 41,96,700/-	Exclusive.
16.	Ferrites (hard)	Electronics		M/s Semiconductors (P.) Ltd., Nagar Road, Poona-14 (1968).	—	—	Non-exclusive. Experimental pilot plant production started.
17.	Heat sealable coating composition	Adhesives		M/s Chandmal Fakirchand Jain, Khajuri Bazar, Indore-2 (1963).	Information awaited.	—	Non-exclusive. Technical aid. Reported to be in production.

1	2	3	4	5	6	7
18.	Hexylresorcinol (57888)	Pharmaceuticals	M/s Unichem Laboratories Ltd., Jogeshwari, Bombay-60 (1964).	No production at present.	13 kg. Rs. 7,800/-	Exclusive.
19.	4-Hydroxycoumarin (62890, 63083)	-do-	-do- (1964).	55 kg. Rs. 11,950/-	72 kg. Rs. 40,000/-	Exclusive.
20.	β-Ionone (77225)	Perfumery, Pharmaceuticals	(i) M/s S. H. Kelkar & Co. (P.) Ltd., Bombay (1964).	—	—	Non-exclusive. The firm is producing the item. According to them, they are not producing it by NCL process.
			(ii) M/s Industrial Perfumes Ltd., Army & Navy Bldg., M. G., Road, Fort, Bombay-1 (1968).	7,625 kg. Rs. 4,75,300/-	—	Non-exclusive. Foreign exchange earned through export of 7600 kg., Rs. 4,73,300/-.
21.	Liquid rubber (60555)	Adhesives, rubber rollers	M/s K. N. Chari & Co., 144, Nyneappa Naick Street, Madras-3 (1962).	No production at present.	2,200 kg.	Non-exclusive. Producing for captive use.

1	2	3	4	5	6	7
22.	Longifolene-utilization of (sponsored)	Perfumery	M/s Camphor & Allied Products, Bareilly (U. P.) (1968).	4·6 tonnes Rs. 3,27,500/-	—	Exclusive. Two perfumery products are manufactured.
23.	Δ^3-Carene-utilization of (sponsored)	-do-	-do- (1968)			
24.	*l*-Menthol from dementholized peppermint oil (sponsored)	Fine chemicals, Drugs	M/S Bhavana Chemicals Ltd., Lakshmi Insurance Bldg., Bombay-1 (1968).	—	—	Exclusive. Experimental adoptation of work in progress.
25.	Nicotine sulphate (45666, 54867, 83716)	Insecticides	M/s Urvakunj Tobacco Bye-products Ltd., Dharmaj (Dist. Kaira) (1963).	5,000 kg. Rs. 1,03,800/,-	15,300 kg. Rs. 1,98,500/-	Exclusive on territorial basis.
26.	Peach aldehyde	Perfumery	M/s S.H. Kelkar & Co.(P.) Ltd., Bombay,(1965).	1,350 kg. Rs. 2,22,200/-	300 kg. Rs. 46,700/-	Non-exclusive. Technical aid.
27.	Phthalates-dioctyl and dibutyl	Plasticizers	M/s Alta Laboratories Ltd., Giri Vihar, Khopoli, (Dist. Kolaba) (1969).	990 kg. (DOP) Rs. 7,400/-	—	Non-exclusive. Production started from Feb. 1969. NRDC agreement in progress.
28.	Polyurethane printing rollers (86991)	Printing	(i) M/s Saraswathy Printing Press, 32, Acharya P. C. Rd., Calcutta-9 (1965)	—	—	Non-exclusive. According to the firm, they are not producing by NCL process.

1	2	3	4	5	6	7
28.	(continued)		(ii) M/s Dabholkar Bros., East Street, Poona-1 (1965).	—	—	Non-exclusive. Experimental production of about 100 rollers of different sizes.
29.	Rigid filters (59608, 66966)	Tube wells	M/s Ashim Filters, 196, Defence Colony, New Delhi (1965).	1,000 mtrs. Rs. 1,83,300/-	1,840 mtrs. Rs. 3,36,160/-	Exclusive.
30.	Rubber base contact adhesive (65977)	Adhesives	M/s K. N. Chari & Co., Madras-3, (1962).	72 ltrs. Rs. 425/-	16,250 ltrs. Rs. 1,32,000/-	Non-exclusive.
31.	Rubber blowing agent	Rubber chemicals	M/s Swastik Rubber Products Ltd., Kirkee, Poona-3 (1968)	18,960 kg. Rs. 1,89,000/- approx.	—	Non-exclusive. Technical aid.
32.	Rubberized cork sheet	Gaskets	M/s Bharat Casements (P.) Ltd., P. B. No. 89, Baroda, (1966)	—	6,49,600 nos. Rs. 3,55,000/-	Non-exclusive. According to the firm, they have modified the NCL process.
33.	Rubber reclaiming agent	Rubber chemicals	M/s Swastik Rubber Products Ltd., Poona-3 (1968).	1,670 kg. Rs. 15,000/- approx.	—	Non-exclusive. Trial production started. NRDC agreement in progress.
34.	Silica gel (sponsored)	Humidity control	M/s Minco Products, 301/27, T. H. Road, Madras-21 (1963).	8,000 kg. Rs. 65,000/-	44,700 kg. Rs. 2,56,000/-	Exclusive.

1	2	3	4	5	6	7
35.	Sisal wax (64958, 65440)	Cosmetics, Polishes	M/s Aphali Pharmaceuticals Ltd., Station Road, Ahmednagar (1966).	Not in production at present.	14,200 kg. Rs. 1,53,200/-	Non-exclusive.
36.	Sorbide nitrate (sponsored)	Pharmaceuticals	M/s Indian Schering Ltd., Mercantile Chambers, Ballard Estate, Bombay-1 (1969).	90 kg. Rs. 2,70,000/-	—	Exclusive.
37.	Styrene DVB-base cation exchange resin (65976, 98155, 98156)	Demineralization of liquids	M/s Industrial & Agricultural Engg. Co. (P) Ltd., 43, Forbes Street, Bombay-1 (1967).	—	—	Non-exclusive. Trial production started.
38.	Thermistors	Electronic devices	(i) M/s Semiconductors (P.) Ltd., Poona-14 (1963).	3,29,450 nos. Rs. 2,80,700/-	18,10,700 nos. Rs. 16,77,000/-	Non-exclusive. Technical aid.
			(ii) M/s Tempo Industrial Corp., Vile Parle (E), Bombay-57 (1963).	9,000 nos. Rs. 36,000/-	8,000 nos. Rs. 33,000/-	-do-
39.	Titanium tetrachloride (sponsored)	Industrial chemicals	M/s Travancore Titanium Products Ltd., Trivandrum-7 (1967).	450 kg. Rs. 3,465/-	—	Exclusive. Trial production started.
40.	Vapour phase chromatograph	Instruments	M/s Associated Instruments Manufacturers (India) P. Ltd., 26-27, Asaf Ali Road, New Delhi, (1969).	5 units Rs. 95,000/-	—	Exclusive. Value is excluding the cost of imported components.

1	2	3	4	5	6	7
41.	Warfarin	Rodenticides	M/S Unichem Laboratories, Bomby (1968).	67 kg. Rs. 39,550/-	—	Exclusive. Production of warfarin started only in 1968.
	Production and value of some of the chemicals Produced in Fine Chemicals Project :					
42.	Alumina chromatographic	Laboratory chemical		400 kg. Rs. 24,500/-		—
43.	Costus root oil	Perfumery		9 kg. Rs. 8,000/-		
44.	Exaltone	-do-		1 kg. Rs. 5,000/-		
45.	Phenoxyacetic acid	Pharmaceuticals		1,360 kg. Rs. 17,000/-		
46.	Silicagel chromatographic	Laboratory chemical		1,318 kg. Rs. 70,000/-		
47.	Sopanox	Soap additive		1,000 kg. Rs. 25,000/-		

SUMMARY OF TABLE I

Year	No. of items manufactured	Value of production (Rs. in lakhs)	Cumulative figure upto the previous year (Rs. in lakhs)
1967—68	29	39·98	51·14
1968—69	47	69·55	91·12

Majority of the items in the Table I refer to import substitution. Assuming 40% of the indigenous production in respect of these items as foreign exchange saving, the approximate saving in foreign exchange due to the production based on the NCL know-how for 1968-69 would be *Rs. 24·5 lakhs.* The cumulative foreign exchange saved on the same basis for the years upto 1968 would be approximately ***Rs. 30·6 lakhs.***

In addition, β-ionone has been exported and the foreign exchange earned during 1968-69 is *Rs. 4·73 lakhs.*

A-XII TABLE II : PROCESSES RELEASED AND AWAITING PRODUCTION

S. No.	Name of the process and Indian patent No.	Field of utilization	Name of the party and year of release	Nature of licence/proposed production/present state of development
1	2	3	4	5
1.	Acetanilide	Dye intermediate	M/s Hindustan Organic Chemicals Ltd., Rasayani, through project engineers M/s R. L. Dalal & Co., Bombay-18 (1966).	Exclusive to project engineers. Estimated production 2000 TPA value Rs. 1 crore. Commissioning runs in progress.
2.	Adhesives for decorative laminates (sponsored)	Laminates	M/s Swastik Rubber Products, Kirkee, Poona-3.	Exclusive.
3.	Alizarin (sponsored)	Dye intermediate	M/s Aniline Dyestuffs & Pharmaceuticals (P.) Ltd., Bombay-1 (1968).	Exclusive.
4.	Aminotriazole (sponsored)	Organic intermediate	M/s Agromore Co., Ltd., Mysore Road, Bangalore-26 (1967).	Exclusive.
5.	Cadmium sulphide photoconductive cells	Electronics	M/s Gera Engineering Co. " Pritam Villa ", 8/352, Boat Club Road, Poona-1 (1969).	Non-exclusive. NRDC agreement in progress.

1	2	3	4	5
6.	Cation exchange resin polystyrene base (74356)	Demineralization of liquids	M/s Tulsi Industries, Poona-3 (1965).	Non-exclusive.
7.	Chlorinated copper phthalocyanine (sponsored)	Dye intermediate	M/s Sudarshan Chemical Industries (P.) Ltd., 162, Wellesley Rd., Poona-1 (1968).	Exclusive. Pilot plant trials in progress.
8.	Covering materials from CNSL (74451)	Chemical resistant flooring	M/s Natson Manufacturing Co., Bhadra, Ahmedabad (1964),	Exclusive.
9.	Diethyl-*m*-aminophenol (sponsored).	Dye intermediate	M/s Sahyadri Dyestuffs and Chemicals (P.) Ltd., 117, Vithalwadi Road, Poona-9 (1966).	Exclusive. 60 TPA capacity planned. Experimental work on pilot production in progress.
10.	Diethylstibestrol (60826, 65778)	Pharmaceuticals	M/s Gluconate Ltd., 23, Camac Street, Calcutta-16. (1965).	Exclusive.
11.	Dithranol	Pharmaceuticals	M/s Indian Dyestuffs Industries Ltd., Kalyan, (1968).	Exclusive.
12.	Vat Golden Yellow GK (sponsored)	Dye intermediate	M/s Amar Dye-Chem Ltd., P. B. 6471, Mahim, Bombay-16 (1967).	Exclusive. Letter of intent now received by the party.
13.	Industrial chemicals from diketene (sponsored)	Organic chemicals	M/s Aniline Dyestuffs and Phramaceuticals Ltd., Bombay-1 (1968).	Exclusive.

1	2	3	3	5
14.	Nonylphenol (sponsored)	Surface active agents	M/s Surfactants (P.) Ltd., 28, Appolo Street, Bombay-1 (1969).	Exclusive.
15.	Opium alkaloids	Pharmaceuticals	Govt. of India, Ministry of Finance, New Delhi (1966).	Exclusive. Capacity planned 4·7 TPA value Rs. 1 crore. Detailed designs of civil, mechanical and electrical works completed.
16.	Perfumery grade geraniol, *citronellal* and *citronellol* (sponsored)	Perfumery	M/s Radhakishan Rajaram & Co. 143, Princess Street, Bombay-2 (1968).	Exclusive.
17.	Phthalates — diethyl and dimethyl.	Plasticizers	M/s Mysore Acetate & Chemicals Co. Ltd., Sri J. W. Road, Bangalore-2 (1968).	Non-exclusive
18.	Recovery of pyridine base	Industrial chemicals	M/s Rainbow Texdyes Corporation, Pratapnagar Road, Baroda (1968).	Technical aid.
19	Radio opaque dyes (sponsored)	Pharmaceuticals	M/s Unichem Laboratories, Bombay (1968).	Exclusive
20.	Sodium cyclamate (sponsored)	Pharmaceuticals	M/s Aphali Pharmaceuticals Ltd., Ahmednagar (1968).	Exclusive

1	2	3	4	5
21.	Terpene G (sponsored)	Perfumery, Insecticides	M/s Camphor & Allied Products, Bareilly (U.P.) (1968).	Exclusive.
22.	Steroids from sugarcane wax (sponsored)	Pharmaceuticals	M/s Brihan Maharashtra Sugar Syndicate Ltd., 980, Sadashiv Peth, Poona-2 (1968).	Exlcusive. Plant designed and fabrication in progress.
23.	Tetrabromoindigo (sponsored)	Dye intermediate	M/s Shree Dyes & Chemicals, Poona-4 (1961).	Exclusive.
24.	Thiodiglycol (sponsored)	Dye intermediate	M/s Hico Products P. Ltd., Bombay (1961).	Exclusive. Not producing for economic reasons.
25.	Vanillin and ethyl vanillin (sponsored)	Pharmaceuticals	M/s Aniline Dyestuffs and Pharmaceuticals Ltd., Bombay-1 (1967).	Exclusive
26.	Vitamin C	Pharmaceuticals	Hindustan Antibiotics Ltd., Pimpri, Poona (1966).	Exclusive. Planning capacity 125 TPA. Designs and specifications of plant and equipment have been completed.

Following processes which have been mentioned under Table I are also licensed on non-exclusive basis to the following additional firms and are awating production :

1	2	3	4	5
1.	DDT-water dispersible	Insecticides	M/s Pesticides Ltd., 28 Sayani Road, Bombay-28 (1967).	
2.	Liquid rubber	Adhesives	M/s Swastik Rubber Products Ltd., Poona-3 (1962).	
3.	Nicotine sulphate	Insecticides	(i) M/s M. M. Patel, P. O. Sunav, Gujarat (1966).	
			(ii) M/s National Tobacco Bye-products, Dal Mandi, Saharanpur (1963).	
			(iii) M/s Tobacco Bye-products P. Ltd., Fort Narasarowpet, Guntur (1963).	Steps are being taken to commission the plant.
4.	Phthalates — dioctyl and dibutyl	Plasticizers	M/s India Carbon Ltd., Ganesh baug, Nehru Road, Bombay-80 (1969), through M/s R. L. Dalal.	Expected to commence production in 1970.

1	2	3	4	5
5.	Polyurethane printing rollers	Printing	(i) M/s United Ink & Varnish Co., P. B. 6862, Vile Parle, Bombay-57 (1965).	Import licence for chemicals applied.
6.	Sisal wax	Cosmetics, Polishes	(i) M/s Shalimar Rope Works, 14, Netaji Subhash Road, Calcutta (1966).	Negotiations with plant fabricators are in progress.
			(ii) M/s Deccan Paint & Chemical Industries, 298, G. T. Road, North Calcutta (1968).	
			(iii) M/s Industrial & Engg. Corpon. 84-B, Bondel Road, Calcutta (1966).	
7.	Styrene DVB-cation exchange resin	Demineralization of liquids	(i) M/s Tulsi Industries, Poona-13 (1963).	
			(ii) M/s Bird & Co. Ltd., Chartered Bank Bldg., Calcutta-1 (1963).	Party not interested in commercialization of the process.
8.	Thermistors	Electronic devices	M/s Adept Laboratories, Karve Road, Poona-4 (1963).	Technical aid.

A-XIII TABLE III : PROCESSES APPROVED FOR RELEASE TO INDUSTRY BY 'PROCESS RELEASE COMMITTEE, NCL'

S. No.	Item	Field of utilization	Production envisaged/yr.	Price Rs./unit	Expected annual turnover Rs. in lakhs	Remarks
1	2	3	4	5	6	7
1.	Aniline	Industrial *chemicals*	600 tonnes	3,090	18·54	Negotiations in progress *through project* engineers.
2.	Butyl titanate	Varnishes & enamels	20 ,,	23,600	4·72	——
3.	Cadmium sulphide photo conductive cells	Electronic instruments	30,000 cells	25	7·5	Released; awaiting production.
4.	Chlorobenzenes (MCB)	Industrial chemicals	10,000 tonnes	1,390	139·00	Now sponsored.
5.	Coating for oil filter paper	Paper	1,700 kg.	16	0·27	Released; under trial production.
6.	Costus root oil	Perfumery	300 kg.	1,100	3·30	——
7.	Dimethylaniline	Industrial chemicals	600 tonnes	8,000	48·00	Negotiations in progress through project engineers.
8.	Ferric oxide oxide (calcined and precipitated)	Catalyst	1,100 kg.	40	0·44	——

1	2	3	4	5	6	7
9.	Double boiled linseed oil substitute	Foundry	1,200 tonnes	2,500	30·00	—
10.	Fructose and chamazulene (108413, 108414)	Pharmaceuticals, Cosmetics	3 tonnes	60,000	1·80	—
11.	*p*-Nitrophenol	Insecticides	300 „	11,000	33·00	—
12.	Optical whitening agents for synthetic fibres	Textiles	5 „	1,05,000	5·25	Negotiations in progress.
13.	*p*-Menthane hydroperoxide	Synthetic rubber	70 tonnes	13,000	9·10	NRDC agreement in progress.
14.	Phenacetin	Pharmaceuticals	100 tonnes	35,000	35·00	Negotiations in progress.
15.	Phenoxyacetic acid	Pharmaceuticals	20 „	18,500	3·70	Negotiations in progress.
16.	Phthalates					
	(i) Dioctyl	Plasticizers	1,500 „	8,000	120·00	In production.
	(ii) Dibutyl	—do—	3,500 „	8,000	280·00	
17.	Potassium ethyl/amyl xanthate	Mineral beneficiation	300 „	10,000	30·00	—
18.	Potentiometric strip chart recorder	Recording instruments	1,200 units	7,500	90·00	NRDC agreement in progress.
19.	Recovery of pyridine bases (113111)	Dyestuffs	—	—	—	—

1	2	3	4	5	6	7
20.	Rubber blowing agent	Rubber chemicals	30 tonnes	13,700	4·10	In production.
21.	Rubber reclaiming agent	Rubber chemicals	100 „	15,000	15·00	In production.
22.	Rubberized cork sheets	Gaskets	5·32 „	21,500	1·14	In production.
23.	Hot and cold sachets	Domestic heating & cooling	1,00,000 sachets	1·50	1·50	—
24.	Sealants for canvas bags	Adhesives	540 kg.	40	0·21	—
25.	Sopanox (di-*o*-tolylbiguanide)	Soap	5 tonnes	25,000	1·25	NRDC agreement in progress.
26.	Staple pins adhesive	Stationery	5 tonnes	20,000	1·00	—
27.	*p*-tert-Butyl catechol	Synthetic rubber	20 „	32,000	6·40	—
28.	Triethyl phosphate	Catalysts	50 „	17,000	8·50	—
29.	tris-Nonylphenyl phosphite	Synthetic rubber	70 „	14,000	9·80	—
				Total	917·67	

A-XIV TABLE IV : PROCESSES READY FOR RELEASE

(A) PROCESSES ALREADY RELEASED ON NON-EXCLUSIVE BASIS

S.No.	Process	Remarks
1.	Anion exchange resin from melamine	Already in production.
2.	Antipriming compositions	Already in production.
3.	Cadmium sulphide photoconductive cells	Licensed to one party; production awaited.
4.	Cation exchange resin polystyrene base	Lincensed to one firm; production awaited.
5.	Coating for oil filter papers	Trial production started by one firm.
6.	DDT-water dispersible	Licensed to three parties; two in production.
7.	Dihydroisojasmone	Already in production by one firm.
8.	Ferrites (Hard)	Licensed to one firm; production awaited.
9.	Heat sealable coating composition	Licensed to one firm; believed to be in production.
10.	β-ionone	Licensed to two firms; one in production.
11.	Liquid rubber	Licensed to two firms; one in production.
12.	Nicotine sulphate	Available on territorial basis.

13.	Peach aldehyde	Licensed to one firm; in production.
14.	Phthalates-diethyl and dimethyl	Licensed to one firm.
15.	Phthalates-dioctyl and dibutyl	Licensed to one firm and a project engineer; one firm in production.
16.	Polyurethane printing rollers.	Licensed to three firms; one in experimental production.
17.	Recovery of pyridine base	Released to one firm as technical aid.
18.	Rubber base contact adhesive	Licensed to one firm; in production.
19.	Rubber blowing agent	Released to one firm as technical aid; in production.
20.	Rubberized cork sheet	Licensed to one firm; in production.
21.	Rubber reclaiming agent	Released to one firm; in production.
22.	Sisal wax	Licensed to four parties; one in production.
23.	Thermistors	Released to three parties as technical aid; two in production.

(B) KNOW-HOW AVAILABLE ON PILOT PLANT SCALE

S.No.	Process	Batch size
1.	Aniline	5 kg/hr. continuous
2.	BON acid	3 kg/batch
3.	*p*-tert-Butyl catechol	10 kg/batch
4.	Butyl titanate	10 kg/batch
5.	Costus root oil	1 kg/batch
6.	Dimethylaniline	9 kg/batch
7.	Dinitromonomethylaniline	50 kg/batch
8.	Double boiled linseed oil substitute	100 kg/batch
9.	Ethylene dichloride	3 kg/hr. continuous
10.	Hexachloroethane	10 kg/hr. continuous
11.	Modified sugarcane wax	5 kg/batch
12.	Monoethylaniline	10 kg/hr. continuous
13.	Nicotine sulphate	Plant designs for processing 1 tonne of tobacco waste
14.	Phenacetine from-*p*-phenetidine	50 kg/batch
15.	Phenoxyacetic acid	50 kg/batch
16.	Phthalates : DBP	25 kg/batch
	: DEP	40 kg/batch
	: DMP	60 kg/batch
	: DOP	60 kg/batch
17.	Rubber blowing agent	10 kg/batch
18.	Rubber reclaiming agent	20 kg/batch
19.	Sisal wax	5 lbs/batch
20.	Sopanox	50 kg/batch
21.	Sorbitol	10 kg/batch
22.	Styrene DVB anion exchange resin	15 kg/batch
23.	tris-Nonylphenyl phosphite	150 kg/batch

(C) KNOW-HOW AVAILABLE ON LABORATORY SCALE

1. Cadmium sulphide photoconductive cells
2. Civetone and dihydrocivetone
3. Coatings for oil filter paper
4. Dihydroambrettolide and Isoambrettolide
5. Exaltolide
6. Exaltone
7. Ferric oxide
8. Ferrites — (Hard and Soft)
9. Fructose and chamazulene
10. 4-Hydroxycarbostyriles
11. *p*-Menthane hydroperoxide
12. *dl*-Menthol from citronellal
13. Neo-lavandulol
14. *p*-Nitrophenol
15. Optical whitening agent
16. Potassium ethyl/amyl xanthate
17. Recovery of pyridine bases
18. Rubberized cork sheets
19. Sealants for canvas bags
20. Stabilized gel for making hot and cold sachets.
21. Staple pin adhesive
22. Triethyl phosphate

Instruments

1. Potentiometric strip chart recorder.

A-XV GENERAL INFORMATION

Recurring budget		*Rs. in lakhs*
1. Pay and allowances		40·70
2, Maintenance & contingencies		6·63
3. Chemicals and apparatus		12·48
	Total	59·81

Capital expenditure		
1. Building		(-) 0·02
2. Equipment and apparatus		1·79
3. Services and miscellaneous		1·44
	Total	3·21

Pilot plant expenditure		
1. Pay and allowances		2·60
2. Raw materials & miscellaneous		1·89
3. Equipment, buildings and services		1·49
	Total	5·98

Total receipts (1968-69)		
1. Analytical services		0·19
2. Technical aid		0·07
3. Sponsored projects		6·22
4. Premia and royalties		0·89
5. CSIR share on account of technical consultancy		0·15
6. FCP sales		2·42
	Total	9·94

Recurring budget for 1968-69	59·81
Percentage of receipts to recurring budget	16·62

Staff strength (1968-69)

1.	Scientific	...	270
2.	Auxiliary technical	...	199
3.	Auxiliary non-technical	...	94
4.	Class IV technical	...	145
5.	Class IV non-technical	...	68
	Total	...	776

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