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Poona

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1967-68

NATIONAL CHEMICAL LABORATORY
POONA

1967-1968

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

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INTRODUCTION

The present report covering the period April 1967 to March 1968 is divided into five chapters. The progress made in sponsored projects, pilot plant projects, product oriented research, and research schemes of applied basic and basic nature is presented in the first four chapters. Service projects and other general information on publications and patents is described in the last chapter. Beginning with this report, the projects in the first four chapters have been assigned permanent identification numbers and these are shown in brackets. These denote the classification (SP – sponsored, PP – pilot plant, ATT – applied time-targetted, AB – applied basic and B – basic) and the year of starting.

During the year under review, 37 sponsored projects (as against 31 in 1966-67) supported by industry, State and Central Government institutions and the PL-480 grant were in progress. Many of these sponsored projects are nearing completion and the project reports will be submitted to the sponsors shortly.

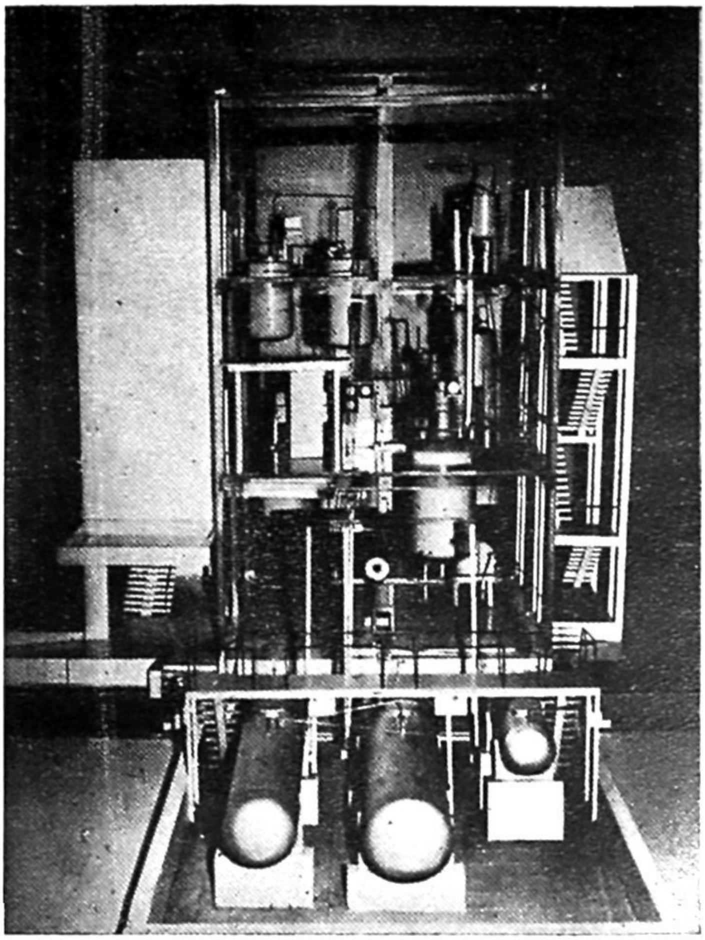
Six pilot plant schemes were in progress. Under a new pilot plant on technical preparation of organic intermediates, know-how for the manufacture of a number of industrial organic chemicals is being developed.

Three tables at the end of this report describe in brief the present position of the various NCL processes. The value of production of 26 processes based on the NCL know-how during the year under report was around Rs. 40 lakhs.

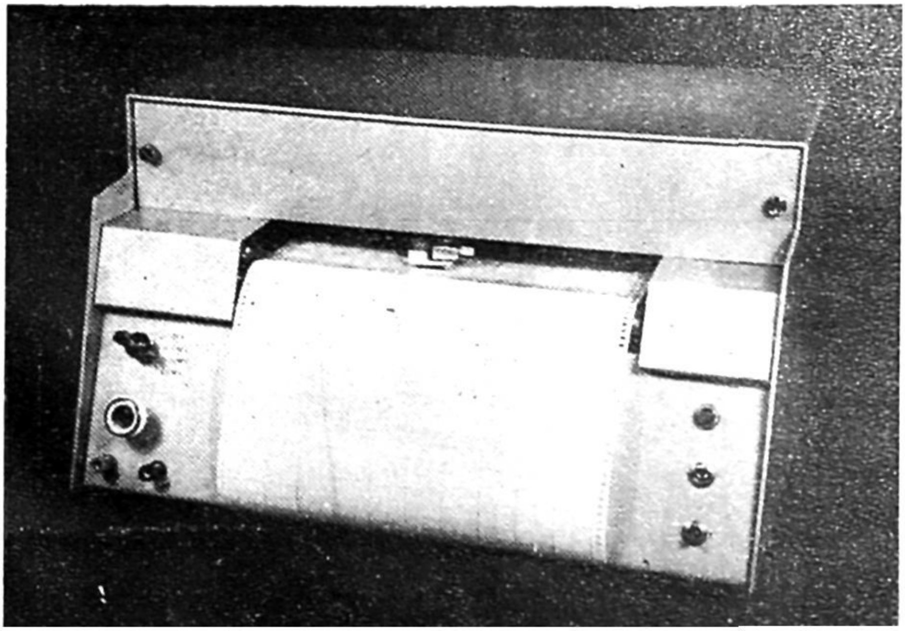
Satisfactory progress has been made by industry in establishing plants based on the NCL know-how for the production of benzoic acid (500TPA), titanium tetrachloride (150 TPA), acetanilide (2000 TPA), vapour phase chromatographs (200 units/y) and calcium hypophosphite (12 TPA). These processes are expected to be on stream in 1968-69.

The Process Release Committee approved the release of the processes in respect of rubber reclaiming and blowing agents, di-*o*-tolylbiguanide, aniline, dimethylaniline, phenacetin, phenlxyacetic acid, tri (nonylphenyl) phosphite, *p*-nitrophenol, *p*-menthane hydroperoxide and potentiometric strip chart recorder, to industry. Several entrepreneurs have shown interest in these projects and it is hoped that these processes will be commercially exploited in the coming years.

It will be seen from the various schemes described in Chapter IV that the Laboratory has maintained an excellent record of basic research. Thus 126 research papers have been published during the year under review. Five new patents have been filed in the period and the total number of patents in force is now 76.



MODEL OF THE ACETANILIDE PLANT



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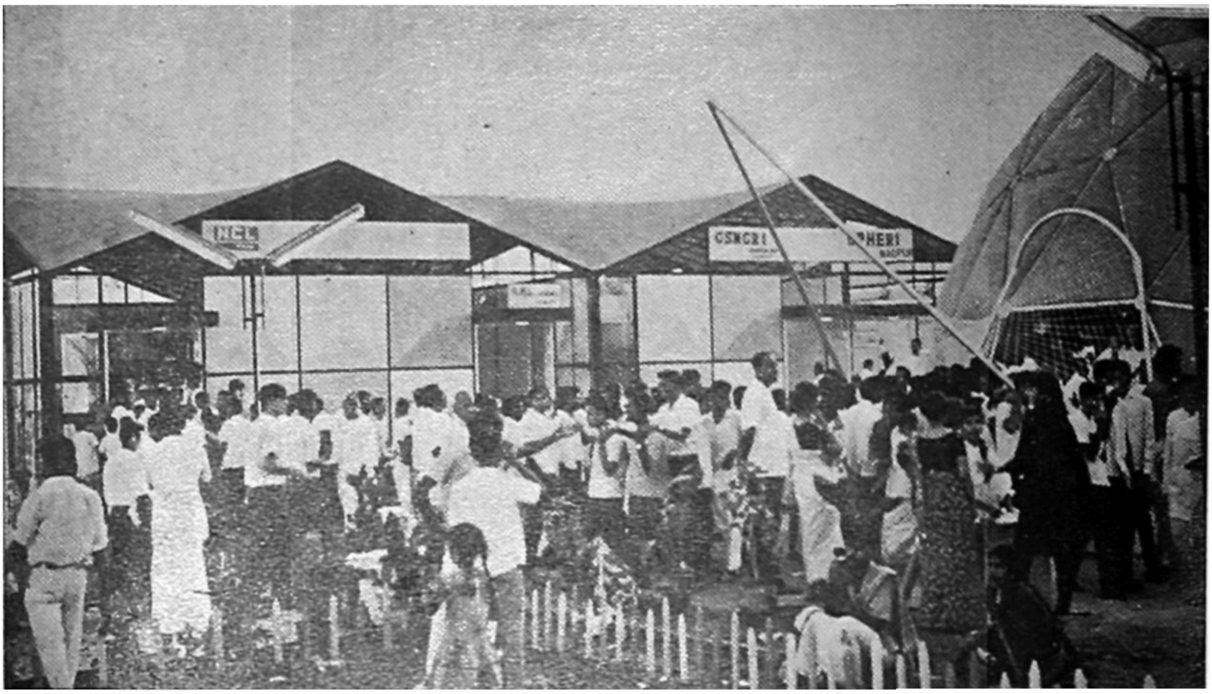
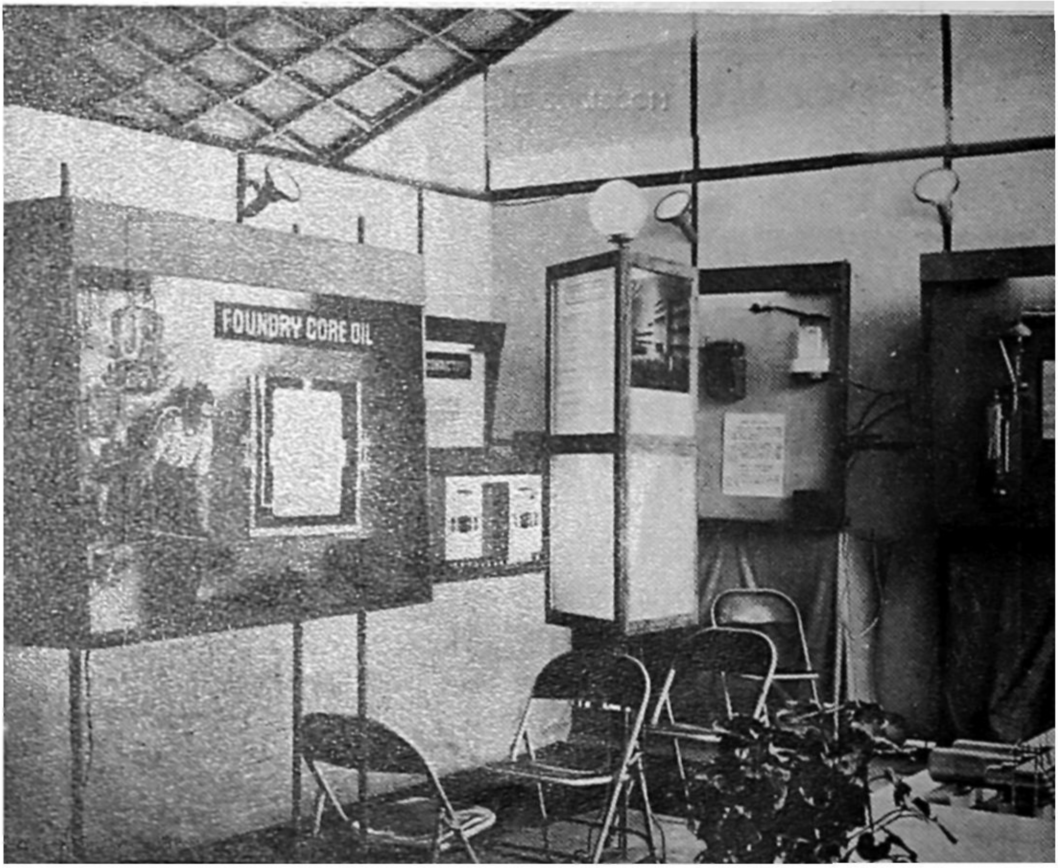


NCL AT THE I.I.T.I.F. EXHIBITION, MADRAS.



INSIDE THE NCL STALL I.I.T.I.F. MADRAS.

SPONSORED PROJECTS

PRIVATE PARTIES

INTERMEDIATES

1. *Benzoic acid :* (SP-40/67)

A project was sponsored for pilot plant investigations on the manufacture of benzoic acid. A suitable pilot plant was set up, using essentially the equipment supplied by the firm, and successful operation of this pilot plant was demonstrated to the sponsor. The extensive data collected on a laboratory scale were found to be reproducible in this pilot plant. This plant has now been shifted to the premises of the sponsor and it is hoped that production of this chemical will be established in the near future. The scheme is concluded.

2. *Industrial Chemicals from diketene :* (SP-5/66)

Ketene and diketene are versatile key intermediates for the manufacure of a number of industrial chemicals. Because of instability, they are not imported; however, our annual requirement of diketene is estimated at 200-300 TPA.

The laboratory investigation on the conversion of acetic acid to ketene was completed. The effect of temperature, pressure and other reaction parameters were studied in relation to product yield and bye-products. The results were analysed and data for optimum runs were collected. This phase of the project is now complete and the design of a larger pilot plant is being considered in the chemical engineering group.

The possibility of using acetone as an alternate starting material was examined, as in the near future it is likely to be available in excess of the country's requirements and at a competitive price.

The laboratory scale preparation of ketene and diketene was therefore carried out using acetone as the starting material. The bench scale unit for continuous conversion of acetone to ketene was installed and operated. Diketene thus prepared was reacted with aniline and *o*-tolidine to give respectively acetoacetanilide and Naphtol AS-G. The products were obtained in satisfactory yields. Further work on the standardization of these preparations are in progress. The scheme is now concluded.

3. *Nonylphenol* : (SP-4/66)

This is an important alkylphenol used in the preparation of ethylene oxide condensates. Import of alkylphenols during 1966-67 was of the order of 3 tonnes.

After standardizing the laboratory scale preparation, on the suggestions from the sponsor, larger scale pilot plant runs were conducted and the data were supplied to the sponsor who is now planning commercial production of this chemical. The scheme is now concluded.

DYES

4. *Alizarin* : (SP-6/66)

Alizarin is largely imported into the country and work on this project was aimed at producing alizarin from indigenously available ' silver salt ' (sodium-2-anthraquinone sulphonate). The various reaction parameters were studied and optimum reaction conditions were standardized. The scheme is now concluded.

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

Chromatographic and spectroscopic methods of analysis have been developed for a few anthraquinonoid intermediates for vat, acid and reactive dyes. The structure of a commercial vat dye has been determined.

6. *Chlorinated copper phthalocyanine* : (SP-7/66)

This is a bright green pigment possessing excellent tinctorial and fastness properties and is widely used in paints, plastics and printing inks. Import of phthalocyanine green during 1966-67 was about 20 lakhs.

The process development studies on the chlorination of copper phthalocyanine to yield a green pigment equivalent to imported samples were completed. The reaction conditions were studied in detail with several indigenously available starting materials and a satisfactory process was finalized and reported to the sponsor. On the basis of our results, the sponsor hopes to set up a full-scale plant for the production of this pigment. The scheme is now concluded.

TERPENOIDS

7. *Improvements in the process for the manufacture of l-menthol from dementholised peppermint oil* : (SP-19/65)

A process for working up of dementholised peppermint oil to obtain the maximum yield of *l*-menthol has been evolved. The sponsor has accepted the process and is implementing the modifications suggested.

A method for conversion of ' liquid menthol ' fraction sent by the sponsor was worked out. It involves oxidation-reduction followed by the preparation of crystalline chloro-acetate.

Several samples of peppermint oil sent by the sponsor were analysed. Four mixtures containing menthol, menthone and menthyl acetate were prepared and analysed by chemical method. The procedure for chemical analysis has been recommended to the sponsor. The scheme is now concluded.

8. *Utilization of longifolene and* $\triangle^3$*-carene :* (SP-15/66)

In continuation of the work reported earlier (Annual Report 1966-67 p. 3), several new compounds derived from longifolene and $\triangle^3$-carene were prepared and submitted to the sponsor for evaluation. Optimum conditions for the preparation of a few compounds approved by the sponsor were established. The sponsor hopes to put into production a few compounds developed as a result of this work.

9. *Utilization of terpene-G :* (SP-17/67)

Pyrolysis of terpene-G was investigated but without any significant results. Chlorination of terpene-G, under specified conditions, yielded a product similar to Toxaphene. Several kilos of this material have been supplied to the sponsor for field trials.

DRUGS AND PHARMACEUTICALS

10. *Calcium hypophosphite :* (SP-2/64)

The process standardized on a pilot plant scale was successfully demonstrated to the sponsor and all the necessary chemical engineering designs have been supplied. The sponsor is putting up a plant for production of this chemical. The scheme is now concluded.

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

Carbimazole, a drug used in the treatment of hyperthyroidism and angina pectoris, is considerably less toxic than most of the drugs used for the same purpose. A synthetic route was standardized yielding a product which conformed to the B. P. specifications in all respects. The work is now nearing completion and will be concluded shortly.

12. *Chemical investigation of ipecac root :* (SP-10/66) (AB-51/68)

The isolation of emetine as well as the conversion of cephaeline to emetine has been worked out on laboratory scale. The scheme has been discontinued since September 1967 as the party could not supply enough plant material.

In the course of the above work two nitrogenous compounds (0.35% yield) were isolated which appeared to be different from the already known constituents. One of the compounds has been taken up for the structural determination and a sample has been sent for pharmacological studies.

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

In commerce, Megimide is also known as Bemegride. This pharmaceutical is used as an antagonist in the treatment of barbiturate poisoning and to terminate barbiturate anaesthesia.

Laboratory scale experiments to standardize various stages in the preparation of this chemical have been undertaken. Small quantities of the drug will be produced to meet B.P. specifications. The developmental work to standardize the process on the scale required by the sponsor will be undertaken after the product obtained meets the specifications.

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

This work was undertaken to develop the know-how for the preparation of some of the more important radio-opaque dyes like Urografin and Biligrafin, in which the main constituents are diatrizoic acid and iodipamide respectively. These dyes cause X-ray contrasts and are essential for radiological diagnosis. The entire need of the country is met by imports at present.

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

Diatrizoic acid and iodipamide were prepared in good yields and scaled-up successfully in larger scale laboratory runs.

A successful process was developed for the reductive methylamination of D-glucose under comparatively lower pressures than reported in literature and excellent yields of methyl glucamine were obtained.

15. *Sodium cyclamate :* (SP-9/66)

The work on sodium cyclamate has been completed and the process handed over to the party. The process has been demonstrated to the party on a 2 kg. scale. The work is now concluded.

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

Isosorbide dinitrate, a coronary vasodilator, is used in the treatment of angina pectoris. It is effective in lowering blood pressure in hypertensives.

Conditions for the technical preparation of the product were established on 1.5 kg/batch scale, based entirely on indigenously available raw materials. Further work to standardize the batch size has been completed to the requirement of the sponsor. The sponsor hopes to start manufacture of this drug based on the process developed.

17. *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.

Conditions for the preparation of sulphacetamide and its sodium salt were standardized on 3kg./batch scale and attempts were made to purify the locally available material to meet the sponsor's specifications.

CATALYLSTS AND INDUSTRIAL INORGANIC CHEMICALS

18. *BD-catalyst* : (SP-1/67)

Preparation of silica-based tantalum pentoxide catalyst, used in the synthesis of butadiene from alcohol-acetaldehyde mixture, was taken up in February 1967. The catalyst was prepared on a laboratory scale and is under evaluation. The recovery of tantalum from spent catalyst is also under investigation.

19. *Calcium silicate :* (*SP*-3/66)

This investigation, was undertaken to standardize a process for the preparation of calcium silicate having bulk density 10-12 lb/cft. As a result of a large number of experiments a satisfactory process has been developed which the sponsor hopes to establish in his Works. The work is now concluded.

PULP AND CARBOHYDRATES

20. *Rayon grade pulp from some species of woods :* (SP-20/66)

Work on the above scheme was completed and details of bench scale results of five different cellulosic raw materials were submitted to the firm.

PERFUMERY CHEMICALS

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

β-Phenethyl alcohol is an important perfumery chemical having an odour of rose. It is widely used in perfumery industries. The entire demand is being met by imports. It is estimated that the demand for this perfumery chemical will be to the extent of 100 TPA.

Laboratory scale preparation of β-phenethyl alcohol has been optimized and the firm hopes to establish production of this chemical. The scheme is now concluded.

22. *Production 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 now being prepared from imported Java citronella oil.

The preparation of perfumery grade geraniol, citronellal and citronellol from Indian lemongrass oil is being investigated.

MISCELLANEOUS

23. *Analysis of organic compositions of industrial importance :* (ATT-21/67) (SP-33/68)

A number of organic compositions available under trade names find special applications in various industries. Many of these are imported. Analysis of these compositions was undertaken on payment by sponsors with a view to explore the feasibility of manufacture of similar compositions from indigenous raw materials.

24. *Steroids and wax from sugarcane pressmud :* (SP-37/67) (AB-20/67)

Several hundred kilos of press mud, (in 50 kg. / batch), supplied by the sponsor, were processed by our new modified method, for the isolation of steroids and a superior quality wax, which were then supplied to the sponsor ing party fori nvestigating their consumer acceptability and market potential.

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

A series of heterocyclic compounds were sent for biological testing. Some of them are undergoing further tests in view of their promissing biological activity.

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

As mentioned in the previous report (Annual Report 1966-67,p.8) work on the following plants has been undertaken; (a) *Boerhavia diffusa* Linn; (b) *Asparagus racemosus;* and (c) *Caesalpinia bonducella.* Of these, interesting results have been obtained with *Asparagus racemosus* and *Boerhavia diffusa.* These studies confirm the pharmacological attributes of these plants. Work on structure elucidation of the pharmacologically active constituents is in progress.

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

The project includes designing and fabrication of electron diffraction equipment and associated accessories. Fabrication of one unit each for Gauhati University, Assam; Fertilizer Corporation of India, Sindri and Defence Science Laboratory, New Delhi, has been undertaken and the project will be wound up by the end of this year, after the deliveries are made.

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

As mentioned in the previous report (Annual Report 1966-67, p.8) work towards the structure elucidation of lac resin has been carried out.

A new lac acid has been isolated as the primary product of base-hydrolysis of lac. Its structure has been elucidated and the compound has been shown to be closely related to jalaric acid.

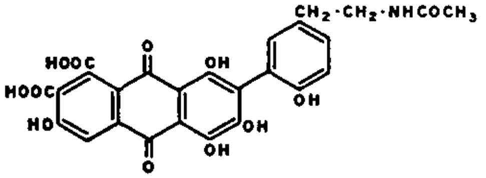
9,16-Dihydroxy-10-keto-palmitic acid has been synthesized and it has been demonstrated that it is one of the products derived from the oxidation-hydrolysis degradation of lac.

Oxidation-hydrolysis degradation sequence has afforded valuable information on the linking of the constituent acids of lac molecule.

To act as reference molecules inter-esters derived from aleuritic acid and epi-shellolic acid are being prepared.

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

The isolation and determination of the constitution of two 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-nitrogeneous laccaic acid B was formulated as (II). These two pigments constitute about 80% of the total dye.



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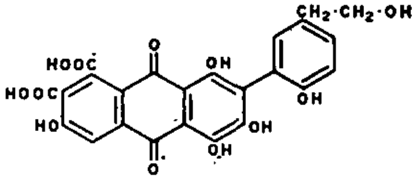


II

Work on the isolation and characterization of other lac pigments has been undertaken. Chromatography of the laccaic acids on a cellulose powder column with butanol : acetic acid : water (6:1:2) as solvent, separated them into two bands, the major band accounting for both laccaic acids A and B. A minor band yielded laccaic acid C, the structure of which is under investigation.

Chromatographic examination of Rangeeni dye (host tree Palas) revealed the presence of a fourth pigment. The structure of this laccaic acid has been proved to be 1, 3, 6-trihydroxy-8-methylanthraquinone-7-carboxylic acid, mainly on the basis of spectral data.

Contrary to the work reported by other workers, the colouring matter of lac larvae does not contain any 'lacciferic acid', but consists merely the laccaic acids associated with protein. The pigments of the ommochrome group may be present in the lac insect as in other insects.

Besides erythrolaccin, two new pigments (desoxyerythrolaccin and isoerythrolaccin) have been obtained from seed lac. These have the structures 3,6,8-trihydroxy-1-methylanthraquinone and 3,6,7,8-tetrahydroxy-1-methylanthraquinone respectively. The structures of both have been confirmed by synthesis; during the synthesis of isoerythrolaccin, a bye-product was another insect pigment isolated by Australian workers.

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

Ilmenite deposits of India are large and are found on the coastaline of Kerala, Kanya Kumari and Ratnagiri. Presently the sponsoring firm is manufacturing TiO_2 pigment by the conventional sulphate process, which uses sulphuric acid and yields the anatase variety of the pigment and a product of comparatively lower purity. In the modern chloride process, TiO_2 is obtained by burning $TiCl_4$ in oxygen. Work on $TiCl_4$ production from Kerala ilmenite was taken up in this laboratory.

On the basis of the work carried out with the unit producing 10 kg. of $TiCl_4$ per hour, a pilot plant unit to produce 500 kg. $TiCl_4$ per day has been designed. Work on the erection of a furnace for the reduction roast of ilmenite ore at about 1100° has been completed in the sponsor's premises at Trivandrum and a few successful preliminary runs have been carried out. The beneficiation unit, consisting of the reduction roast furnace and tanks for acid leaching of the reduced charge, will handle about one tonne per day of the ore. The pilot plant unit at Trivandrum is expected to go on stream shortly.

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

Work on Kashmir soft woods by various processes including acid sulfite pulping was completed and pilot plant trials are being carried out. Resulting pulps are being tested for tyre cord spinning.

32. *Investigation of mixture of hard woods from Bastar forest for dissolving pulp :* (SP-38/67)

Work on the above scheme was completed and details of investigation were communicated to Preinvestment Survey of Forest Resources, Ministry of Food & Agriculture, Government of India, for scrutiny by foreign experts.

PL-480 SCHEMES

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

Thermodynamic properties of refractory materials (useful in ceramic industry and in the industry associated with the development of atomic energy at high temperatures) are being studied by employing transpiration and Knudsen cell effusion techniques.

(a) The vapour pressure of $MnCl_2$ was determined between the temperatures 993-1218°K employing a transpiration technique. The second law calculations yielded for the heat of vaporisation $\triangle H_{298}$ a value 52.41 ± 1.27 Kcal. which compared favourably with the third law value 54.52 ± 0.78 Kcal.

(b) The equilibrium reaction $Mn_{(c)} + MnCl_{2(g)} \rightleftharpoons 2MnCl_{(g)}$ between 1243-1413°K was investigated by a flow method. Over the temperature range the $\triangle H_r$ was found to be 57.74 ± 1.64 Kcal. The $\triangle S_{r1328}$ was 22.83 ± 1.24 cal./deg.

(c) Using similar technique as above the vapour pressure of nickel chloride was determined between 1030-1116°K The vapour pressure equation is represented as $\text{Log } P_{(\text{atm.})} = \frac{-11{,}277.3 \pm 322.66}{T} + 9.060 \pm 0.3$. The calculated heat of vaporization is 58.11 ± 1.47 Kcal. which compares well with that of third law value of 58.16 Kcal.

(d) The equilibrium reaction $Ni_{(c)} \pm NiCl_{2(g)} \rightleftharpoons 2NiCl_{(g)}$ was studied over the temperature range 1278-1380°K. $\triangle H_{r_{1329}}$ is found to be 97.1 Kcal. and the entropy of reaction $\triangle S_{r_{1329}}$ is 58.3 cal deg.$^{-1}$.

(e) In the literature it is reported that nickel aluminate can be prepared by heating a mixture of finely gound pure nickel oxide and alumina at 1000° and above for several hours. The spinel was prepared by the interaction of gaseous aluminium trichloride with nickel oxide. The equilibrium study was carried out between 1270°K and 1448°K by using transpiration technique. In this reaction gaseous aluminium oxychloride was observed. The overall reaction is repsesented by the equation

$$6NiO_{(c)} + 4AlCl_{3(g)} = NiAl_2O_{4(c)} + 5NiCl_{2(g)} + 2AlOCl_{(g)}$$

From the experimental results, the estimated value for $\triangle Hr$ (heat of reaction) at 1360°K is 201.2 Kcals. and the corresponding entropy $\triangle S_r$ 138.94 cal deg.$^{-1}$.

(f) Solid AlOCl was found to decompose as $3AlOCl_{(c)} = AlCl_{3(g)} + Al_2O_{3(c)}$ between 450-650°. From this reaction the heat of dissociation was found to be + 42.4 Kcal. mole^{-1}. Employing this value, the heat of formation of AlOCl was caculated as –190 Kcal. mole^{-1} which agrees with the values already reported in the literature.

High temperature vacuum microbalance : A silica beam microbalance has been fabricated to study vaporization of tungsten carbide and the rare earth sulphides at about 2000°. A graphite resistor vaccum furnace suitable for vaporization studies has been designed, fabricated and erected. The assembly consists of a microbalance mounted on the graphite furnace. The unit is enclosed in a vacuum system which can be easily evacuated to a vacuum of about 10^{-4} torr at a temperature of 1800° inside the furnace. The microbalance is being standardized to yield reliable data.

34. *Work on investigations 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 interesting phenomenon of water evaporation retardation by means of monolayers of saturated long chain fatty alcohols and their derivatives spread over the water surface is now well known. Under the programme of the present project, basic studies of the various physical properties of these compounds in monolayer and bulk state have been undertaken in order to evaluate the efficacies of the various films as water evaporation retardants.

Direct condensation of ethylene oxide with stearyl alcohol and cetostearyl alcohol mixtures to obtain corresponding alkoxy ethanols was tried in order to develop a cheap process for the preparation of alkoxy ethanols on a large scale for use as water evaporation retardants. Condensation products obtained at reaction temperatures between 115° and 155° were analysed and found to contain 15-20 per cent of the monocondesates, 60-70 per cent unreacted alcohols and 15-25 per cent of polycondensates. Both distilled and undistilled products were evaluated as water evaporation retardants in the evaporimeter pans in the open. Ethylene oxide (1mole) condesation product of cetostearyl alcohol was found comparable to the corresponding alcohols and synthetic mixture of alcohol and alkoxy ethanols as water evaporation retardants. The condensation product with 0.5 mole ethylene oxide exhibited superior efficacy as compared to pure alcohols and was only about 6-8 per cent less efficient than the pure octadecoxy ethanol. Pure alkoxy propanols and butanols were prepared from n-long chain alcohols by Williamson's method in 99.9 per cent purity. Efficacies of these compounds are being investigated in evaporimeter pans in the open air. Evaporimeter studies and petri dish experiments have been continued on various ethylene oxide condensation products as well as synthetic mixtures of alcohols and alkoxy ethanols.

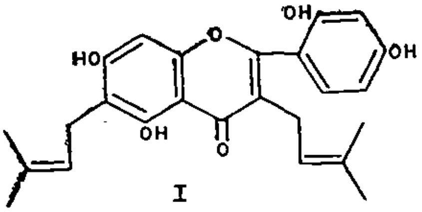
Surface viscosity measurements of monomolecular films of n-alkoxy ethanols (C_{16} to C_{22}) were continued to study the effect of intermolecular interaction and phase transformation at various temperatures and pressures. Surface potential measurements were continued on C_{16}-OC_2H_4OH, C_{18}-OC_2H_4OH, C_{20}-OC_2H_4OH and C_{22}-OC_2H_4OH films at three different temperatures and as a function of film pressure and area per molecule. π-A isotherms of mixed monolayers of alcohols and alkoxy ethanols were continued for different temperatures. In order to investigate the spreadability on the addition of ethylene oxide units to the polar group, measurements on the rate of spreading were undertaken for C_{18}-$(OC_2H_4)_2OH$ and C_{18}-$(OC_2H_4)_3OH$ films.

Heats of mixing were measured for methylcellosolve-water, methylcarbitol-water at 35° and 45°. These results showed that the enthalpy of mixing ΔH^M decreases as the temperature increases from 35° to 45°.

Surface tension measurements were carried out for n-long chain alcohols in the temperature range 45°-95°. From these data, relevant thermodynamic properties have been calculated. Dielectric constant measurements were undertaken in the frequency range 0.5-100 Kcs between 25° and 100° for C_{16}-OH, C_{18}-OH, C_{20}-OH and C_{22}-OH to obtain information on molecular rotation in the different phases of their solid state.

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

The stem and root bark of *Morus alba,* which have not been so far examined, contain four new flavones with the following structures :



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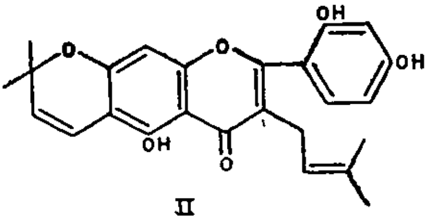

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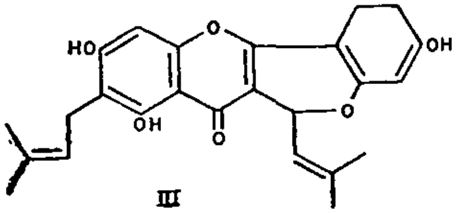

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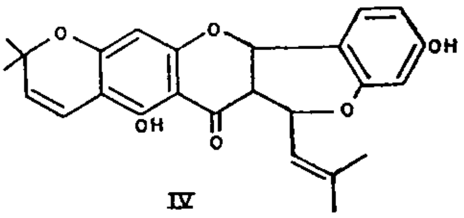


IV

The heartwood of *Morus alba* has furnished resorcinol and two other phenolic compounds, the structures of which are under examination.

From the bark of *Pinus longifolia* catechin, texifolin and two known flavonoid glycosides, quercitrin and afzelin were isolated; no flavonoid glycoside has been isolated so far from a pine.

From the acetone extract of *Pinus excelsa* bark, taxifolin has been isolated.

An investigation of the bark of *C. hystrix* has revealed the presence of friedelin besides a few unidentified triterpenoids which will be investigated.

From the bark of *Picea simithiana* a few flavones have been isolated in small amounts and their identification is in progress. A preliminary examination of the bark of *Picea morinda* has shown the presence of a few flavonoids, and these are being isolated.

From the heartwood of *Quercus lamellosa* ellagic acid and gallic acid have been isolated.

From the heartwood of *Artocarpus lakoocha* artocarpin, cycloartocarpin, resorcinol and 2,4,3′,5-tetrahydroxystilbene have been isolated. β-Resorcyclic aldehyde, 3,5,4′-trihydroxy stilbene and 2,4,3′,5′ tetrahydroxystilbene were isolated from an old specimen of *A. lakoocha* of uncertain origin. The heartwood of *A. chaplasha* has yielded artocarpin, cycloartocarpin and two other flavones which appear to be new.

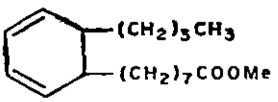
Tissue culture : Teak, *Artocarpus*, mulberry and *Populus* tissues have been grown in culture. All these tissues grow well on synthetic media. Artocarpanone has been found to be present in *Artocarpus* tissues. The tissues of *Populus nigra* grown on a synthetic medium contain a colourless crystalline compound of molecular formula $C_{32} H_{50} O_4$. It appears to contain an acetate group, a five membered lactone or ketone and an isoprenyl group. Further work to elucidate its structure is in progress. The structure of a yellow crystalline compound isolated from teak tissues grown in third sub-culture is being investigated.

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

It has been reported earlier (Annual Report 1966-67, p. 15), that mild thermal treatment of methyl eleostearate, in presence of a catalyst, resulted in ~ 30 % conversion to the primary cyclic monomer (methyl cycloeleostearate, I). When(I) is exposed to a higher temperature (~200°), it is almost completely transformed to a new isomer (cyclic monomer-II), which has been shown to be (II). It has also been found that uncatalysed thermal treatment of methyl eleostearate at the higher temperature (240°) affords the dimer in good yield.

It has also been demonstrated that cyclized tung oil is an excellent stationery phase for gas liquid chromatography.

The mechanism of genesis of eleostearate dimer has been elucidated. The useful malenization reaction has been amicably applied to the dimer.



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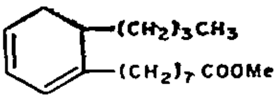

II

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PILOT PLANTS

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

Large quantities of this basic organic chemical are being imported in the country. Imports for 1966-67 were of the order of 2647 tonnes valued at Rs. 53 lakhs. Aniline is listed in the manufacturing programme of M/s Hindustan Organic Chemicals, who will be putting up a 600 TPA plant. The projected demand for aniline at the end of Fourth Plan is 9000 TPA. Thus there will be sufficient scope for further capacity of aniline in the country.

A 5kg/hr. pilot plant for the continuous vapour phase hydrogenation of nitrobenzene to aniline was operated successfully. An indigenously prepared catalyst was used throughout these trials. During the several runs carried, a consistent yield of over 98% was obtained. Continuous testing of the catalyst is in progress. A proposal to shift the pilot plant to HOC's Rasayani site for catalyst evaluation on a larger pilot plant is under consideration.

2. *Chlorination and hydrochlorination of ethylene* (PP-3/63) (ATT-93/68)

Trichloro- and tetrachloroethylene : These are versatile organic solvents used for various industrial purposes. The present largest use for tetrachloroethylene is in the dry cleaning of garments.

Although manufacturing licenses for these chemicals have been given to a few firms, these are not still made in the country. Imports of trichloro- and tetrachloro-ethylenes during 1966-67 were 99 tonnes valued at Rs. 1.8 lakhs and 1632 tonnes valued at Rs. 23 lakhs respectively. Demand for these chlorinated ethylenes is estimated at 15,000 TPA valued at Rs. 2.25 crores by 1970.

Earlier, chlorination of ethylene in a fluidized bed catalytic reactor was attempted wherein a mixture of a number of chloro-ethylenes was obtained. The results were found to be inconsistent with the yields of trichloro-compounds.

A new route is being worked out wherein ethylene dichloride is used as a starting material to obtain mainly trichloroethylene. A new type of reactor has been developed. This pilot plant project is now discontinued and work on the new route is being continued as a time-targetted project.

Ethyl chloride : Ethyl chloride is an important intermediate for the manufacture of tetraethyl lead, an additive in petroleum fuels as antiknock agent. Imports of ethyl chloride during 1966-67 were nearly 42 tonnes valued at Rs. 1.7 lakhs, while the estimated demand is placed at 3000 TPA.

On the basis of the laboratory scale experiments on the hydrochlorination of ethylene a bench unit of 1 kg./ hr. capacity was worked and data have been obtained. It is proposed to set up a larger unit in collaboration with industry, where both hydrogen chloride and ethylene are readily available.

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

These are widely used plasticizers in the plastics industry. Although some quantity of these is indigenously produced, the major requirement of the country is still met through imports. During 1966-67, 788 tonnes of dimethyl phthalate valued at Rs. 28 lakhs and 2675 tonnes of dioctyl phthalate valued at Rs. 66 lakhs have been imported. The estimated requirement in 1970 for DMP and DEP is about 18,000 TPA

The NCL process for dioctyl phthalate and dibutyl phthalate was demonstrated to M/s R. L. Dalal & Co., Bombay, who are engineering the plant. Since carrying out this demonstration the process has been further improved in the light of the industry's demand for a product with colour specifications superior to those given by ISI. The process as it now stands gives DOP of 20 Hazen units (colour). The yield figures based on phthalic anhydride and alcohol are also comparable to those reported by several firms manufacturing this plasticizer.

A complete report on the processes for DMP and DEP has been handed over to M/s Mysore Acetate & Chemical Co. Ltd., Bangalore, who are expected to put up a plant based on this process shortly.

4. *Dissolving Pulp* : (PP-2/58)

All the mills producing rayon filament yarn in India except one are using imported pulp for rayon yarn manufacture. Similarly, three tyrecord manufacturing units also depend on imported pulp, and no indigenous cellulosic raw material is utilized for the production of above grades of pulp. There is a real need, therefore, to develop processes for the production of above grades of pulps.

With this aim in view, work on *Eucalyptus hybrid* (Madras State) was undertaken, and a study was completed of its treatment by the acid prehydrolysis sulphate process. Pulps obtained by bench-scale as well as pilot plant scale studies were both sent for testing by outside parties. The report on our pilot plant trial pulp is given below :

1. α-Cellulose	93.44%	2. Hemi-cellulose	7.45%
3. β-Cellulose	6.04%	4. γ-Cellulose	1.01%
5. 1% NaOH solubles	1.54%	6. 7.14% NaOH solubles	6.44%
7. Alcohol-benzene (1:2) solubles	0.19%	8. 18% NaOH solubles	3.26%
9. 21.5% NaOH solubles	2.6%	10. Pentosan	1.56%
11. Ash	0.129%	12. Silica	46 ppm
13. Iron	43 ppm	14. R_{203}	10 ppm
15. Copper number	0.285	16. Viscosity (1% cuprammonium) Cp.	16.6
17. Brightness - (elrepho)	82		

Pulp of these chemical properties when tested at the laboratary showed good filtration of viscose, and the yarn spun out of it had good strength.

A two-stage alkali pulp from the low temperature series, when processed with imported soft wood sulphite pulp in 80:20 proportion, gave filtrability values of viscose equal to sulfite pulps. Bamboo pulp (TSA process) by using 37% CS_2 in xanthation gave a pulp comparable with imported viscose rayon pulp. Bench-scale work on the preparation of micro-crystalline cellulose powder was completed and the powder was found suitable for thin-layer chromatography.

The acid prehydrolysis sulphate pulps from *Eucalyptus hybrid* and bamboo were upgraded to 96% α-cellulose content. Testing of these pulps for tyrecord spinning is continued.

Experiments in the use of mixed woods for the preparation of RG pulp are in progress.

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

Fine chemicals (both organic and inorganic) are being regularly supplied on order to various research organisations - private and Government.

About 300 chemicals are regularly prepared and steps are being taken to include more chemicals for preparation which are now being imported. A separate shed for the preparation of silica gel and alumina has been constructed. With this facility it will now be possible to fulfil the requirements of these adsorbents.

Comparative figures of production and sale values of the unit during the period 1965 to 1968 are tabulated below :

Year	*Production* Rs.	*Sales* Rs.
1965-66	1,30,148	86,966
1966-67	2,82,821	1,86,597
1967-68	2,07,511	1,46,225

6. *Technical preparations of some organic intermediates :* (PP-6/67)

Optimum conditions for the preparation of industrially important organic chemicals such as *p*-nitrophenol, 2,4-dinitro-N-methylaniline, trinonylphenyl phosphite (Polygard), triethyl phosphate, *ter*-butylcatechol, potassium ethyl xanthate and potassium amyl xanthate, pure anthracene and carbazole from coal tar, crude anthracene, di-*o*-tolyl biguanide (Sopanox) and guaicol from *o*-anisidine were arrived at after exhaustive experimentation. Pilot plant trials on the preparation of these chemicals are in progress.

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PRODUCT ORIENTED RESEARCH

1. *Preparation of photoconductive cells :* (ATT-2/66)

Cadmium sulphide photo cells show a large change of resistance for small changes in light intensity and hence simple circuits can be designed which can be made to respond to light signals. Some of the important applications are (1) light sensitive relay, (2) industrial safety devices and controls, (3) sound reproduction, (4) camera exposure meters and (5) scientific instruments.

Starting from CdS, a composition has been developed to obtain photosensitive crystals by sublimation process. Photoresistors so developed show a change of four to five orders of magnitude in resistivity on illumination. They compared well with similar imported samples.

The construction of an improved furnace is in progress. This will have double the capacity (150 crystals per batch) of the existing furnace , and will provide more data on the economic aspect. A data sheet and application note have been prepared and are being sent to interested parties. Fabrication of devices has also been taken up with a view to demonstrating the applications.

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

Tin oxide resistors have recently been developed for high quality high reliability applications. Their low current noise and excellent frequency characteristics make them especially suitable for power supply filter circuits, power amplifier circuits or other functions where their rugged construction and stable performance can be used to advantage at low cost.

Thin films of tin oxide have a great potential in the electronic industry for high temperature and high voltage resistors. Demand for these resistors is growing with the development of defence electronic industry, where these are mainly applied.

A number of processes for deposition of tin oxide conducting films on ceramic substrates have been tried out, and the conditions for obtaining stable low resistance deposits are being studied. It is proposed to develop a continuous coating process based on a suitable deposition technique.

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

In recent years ferroelectric ceramics are finding increasing industrial applications as transducers for the generation of sonic and ultrasonic waves. The prevailing opinion indicates that piezoelectric ceramics can be made only from ferroelectric materials. Although there is a steady increase in the list of ferroelectric compounds, not many are suitable in ceramic form, for use as electromechanical transducers. The present investigation is aimed at preparation of some ferroelectric ceramics of a new and improved type, and a detailed study of their structural and other characteristics in relation to their ferroelectric and associated piezoelectric properties. Some doped lead titanate ceramics of general formula $Pb\left[La_{0.5}(B_{II}^{5+})_{0.5}\right]_xTi_{1-x}O_3,$ where $B_{II} = Nb$ or V were prepared.

Study of the above types of doped lead titanate ceramics was continued. The chief figure of merit used to evaluate the piezoelectric properties of the ceramic disks was the radical coupling coefficient. This has been determined by maximum and minimum impedance measurements and values have been calculated using the relation $k_r/(1-k_r^2) = 2.51\,(f_a - f_r)$, where f_a and f_r are radial antiresonance and resonance frequency respectively. It has been observed that doping materials play an important role on the piezoelectric properties of the ceramics. The value of the radial coupling coefficient increased according to the increase of doping material concentration and reached a maximum with $X = 0.15$.

The lattice parameters for all the compositions at room temperature were determined on the basis of X-ray powder diffraction patterns. The effect of small proportion of La and Nb or La and V as doping material in the composition (upto $X = 0.10$) appeared to decrease the tetrahedral distortion with a decrease of Curie temperature and increase of spontaneous polarization values. The lattice dimension a_0 expanded rather slowly as X increased until the composition $X = 0.10$ was reached and tatragonal symmetry was retained. Beyond this composition a_0 suddenly expanded to a large value and a change over to orthorhombic symmetry was observed.

4. *Thermoelectric semiconductors :* (AB-64/68)

Based on the basic work already completed under this project new system using $Bi_2Te_3 - Bi_2Se_3$ and $Bi_2Te_3 - Sb_2Te_3$ doped with suitable impurities were prepared. Polycrystalline thermoelctric elements (P and N-type) have been prepared under controlled conditions.

In order to find their suitability in thermoelectric device fabrication, an experimental set-up for measuring their physical properties such as electrical conductivity (σ), thermolectric coefficient (α), thermal conductivity (k) and figure of merit (z) at different temperatures (-180° to 100° approximately) is being installed. Arrangements have been made to extend the said work for studying these properties under controlled magnetic field.

Accordingly, for accurate measurements of the magnetic field strength, magnetic susceptibility of a few known compounds was measured at room temperature. Our preliminary results indicated a field strength of the order of 3000 oersteds which could be conveniently applied across the specimen.

5. *Posistors :* (ATT 62/68)

The aim of the work was to investigate semiconducting properties of $BaTiO_3$. The unique phenomenon of PTCR (positive temperature coefficient of resistivity) anomaly of semiconducting $BaTiO_3$ has opened up a wide field for applications in electronic engineering.

An attempt has been made to probe into PTCR behaviour by studying various semiconducting properties of $BaTiO_3$ such as electrical conductivity thermo e. m. f., a. c. characteristics, rectification and barrier layer capacitance phenomena etc. Several compositions from the two new systems (i) $Ba_{1-x}Er_xTiO_3$ and (ii) $Ba_{1-x}Tb_xTiO_3$ have been prepared. The main object of the invention was to find out a new composition of "posistor" yielded by higher percentage of doping and giving higher value of temperature coefficient of resistivity (α). This was achieved by doping 0.5 mole % of erbium and 0.3 mole % of terbium.

The highest value of $\alpha_{max.}$ reported so far is about 60% per degree. With the new compositions the values obtained were 80 % per degree for erbium and 61% per degree for terbium materials.

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

Silicon diodes and transistors have almost completely replaced the old germanium devices. In India several firms have already started manufacturing silicon devices from the imported raw materials. To meet the requirements of these industries, it is estimated that about 500 kg. (value Rs. 15 lakhs) of polycrystalline silicon will be required per year.

The unit for the preparation of silicon tetrachloride set up earlier was run successfully during the year to meet the laboratory's requirements.

A unit for the preparation of trichlorosilane, a valuable starting material for silicon products, has been set up and several runs have been taken successfully. Dry HCl gas was passed on to ferrosilicon contained in a vertical silica reactor maintained at 300-400°. The product was collected in a series of condensers maintained at solid CO_2 temperature. The condensate was fractionated to obtain pure $SiHCl_3$. Dry HCl gas was prepared by burning hydrogen in an atmosphere of chlorine in a specially constructed burner.

Effect of variation in hydrogen : chlorine ratio in the feed gas, temperature of the ferrosilicon and also the use of some suitable catalysts are being investigated.

A laboratory unit for the reduction of silicon tetrachloride to polycrystalline silicon has been set up and run successfully. The reduction of trichlorosilane will be tried in the same set up and the performance of the two methods compared.

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

Soft ferrites find extensive application in the manufacture of high frequency cores, radio antenna rods, filters, H. F. chokes, fly back transformers, deflection coils etc. Nickel zinc soft ferrite containing excess iron and a small amount of Co^{2+} together with some other trivalent ion such as Cr^{+2}, Mn^{+3} or Al^{+3} have been prepared and studied. Compositions with high μ, Q and f have been prepared by a proper control of :

(a) the purity and particle size of the starting material,
(b) the composition and stoichiometry of the final product and
(c) post-firing annealing under a suitable atomosphere.

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

The decomposition of some iron salts was studied thermogravimetrically with a view to find out an easily decomposable material which could be wet reduced in oil below 250°. Ferrous oxalate and ferric oxalate showed some promise as these two compounds were found to get decomposed in air at 220° and 190° respectively. However, this was found to happen only in the presence of oxygen (even in traces) when decomposition set in almost immediately with dehydration, thus showing only a single step in the thermogram. In the absence of oxygen, the dehydration was followed by a distinct and stable anhydrous phase, thus showing a second step in the thermogram corresponding to the decomposition of anhydrous ferrous oxalate at 340° and that of anhydrous ferric oxalate at 320°. The reduction of formates of iron was also found to get completed above 250°.

The oxides of iron obtained by the decomposition of these formates and oxalates of iron were found to posses some interesting ferromagnetic properties which need further investigation.

The precipitation of copper salt solutions with alkali carbonates has been reported to result in a variety of basic copper carbonates. Investigations now carried out showed that most of the changes in composition take place during washing. This has been traced to the fact that the first precipitate formed at higher pH (9.3–10.8) and at higher concentration of the alkali carbonate (above 1N) tended to be in the form of a crystalline double carbonate with the alkali used. The formation of this double carbonate is also aided by good stirring. During washing of the alkali carbonate from this double carbonate, the pH rose locally in the vicinity of the precipitate, thus causing changes in its basic character which are difficult to control. At concentrations not exceeding 1N, a gelationous precipitate of basic carbonate is generally formed which tends to be more basic with rise in pH.

Thermogravimetric studies on the mixed nickel zinc oxalates in air and hydrogen showed that the decomposition proceeds through two distinct steps : (1) due to dehydration between 130° to 240°, and (2) due to decomposition between 325° to 415°. The end product of decomposition in air was a mixture of oxides while that in hydrogen corresponded to a mixture of nickel metal and zinc oxide. The latter is being confirmed by X-ray studies. Differential thermal analysis of the oxalate mixture in air showed three peaks : (1) endothermic peak between 200°-250° due to dehydration, (2) two exothermic peaks due to decomposition, and (3) further oxidation of carbon monoxide to carbon dioxide.

Catalyst supports such as alumina, silica gel and zinc oxide were prepared under controlled conditions and their physical and surface properties are being evaluated.

Surface areas of a large number of potential chromatographic adsorbents such as oxides, carbonates and silicates of calcium and magnesium were measured by the BET technique. The silicates in general had large surface areas. Surface areas of a number of catalyst samples were also evaluated.

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

In the Get–Together of Research & Industry held in December 1965, a five year programme of research and development on silicone fluids, grease and rubber was suggested. Accordingly, work on the preparation of monomers and intermediates has been undertaken at this laboratory. Subsequent development of suitable formulations of oils, grease etc. will be done at Indian Institute of Petroleum, Dehra Dun.

Accurate estimates of present demand of silicone products in the country are not available. It is learnt that one firm produced 32 tonnes of finished silicones, valued at Rs. 11 lakhs in 1964-65. Annual consumption of these products is estimated at 50 TPA which is likely to go up steadily.

After preliminary literature survey and upgradation of the indigenously available ferro-silicon, alternative synthetic routes for organosilanes were examined in the first half of the year, which included trial modifications of the Rochow and Grignard procedures and a reported direct reaction of a mixture of methyl chloride and silicon tetrachloride on aluminium metal powder suspended in a $NaCl$-$AlCl_3$ melt. Subsequent experiments were restricted to the Rochow reaction of methyl chloride on silicon, and the Grignard reaction of the phenylmagnesium compound on silicon tetrachloride. Alternative designs of the reactor were tried in Rochow procedure to secure high values of conversion of methyl chloride gas. The step involving impregnation of the copper catalyst was also eliminated. The commercial methyl chloride so far available was very impure, and some of the experimental data now collected are sure to be modified on arrival of the pure gas from a new Indian manufacturer shortly. Experiments to replace bromobenzene with the cheaper chlorobenzene in the Grignard synthesis met with partial success.

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

Laboratory data on butyl titanate have been collected. Some pilot plant runs were taken and few more are under way to finalize the process.

11. *Synthetic inorganic chemicals :* (ATT-14/64)

11.1 *Chromatographic adsorbents :* The surface area studies of the less frequently used adsorbents showed that magnesium trisilicate has the largest surface area (200 m^2/g). Further detailed study of magnesium trisilicate such as temperature and method of activation, determination of bulk density, specific gravity, sieve analysis etc. has been done. Acid washed magnesium trisilicate was also prepared and its properties determined.

11.2 *Magnesium perchlorate :* Experiments were carried out to standardize conditions to obtain the desired needle-shaped crystals of magnesium perchlorate. Dehydration of the hexahydrate under vacuum by controlling the heating rate has been done to obtain the dihydrate. Samples tested in the microanalytical laboratory showed satisfactory performance.

11.3 *Ascarite :* A number of trial experiments were conducted. Compositions and blending temperatures were varied widely. In the initial stage, imported asbestos was used and this was subsequently replaced by Indian asbestos with success. Microanalytical test report on the material is satisfactory.

Preparation of the above mentioned materials was carried out (to meet the demand for FCP sale).

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

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. Indigenous demand for the material is being assessed.

Several successive runs on the pyrolysis of Freon 22 (chlorodifluoromethane) gave tetrafluoroethylene at good rates of conversion (about 40%) around 700°. Higher conversion rates produced considerable amounts of hydrogen fluoride and other by-products.

$$CHClF_2 \xrightarrow{700^\circ} CF_2 + HCl$$

$$2CF_2 \longrightarrow CF_2{=}CF_2$$

The reactions were carried out in a special graphite reactor with cooling arrangements. The resultant tetrafluoroethylene was collected over water. Analysis by mass spectrometer showed that the collected gas was nearly pure tetrafluoroethylene (mass = 100).

Some modifications in the reactor are being introduced to avoid corrosion and erosion possibilities.

13. *Di-o-tolylbiguanide* : (ATT-22/66)

The chemical is widely used as antioxidant for soaps and other cosmetics under the commercial name ‘Sopanox’.

Following the optimized bench scale conditions for the condensation of *o*-toluidine and dicyandiamide, reported earlier, for the preparation of *o*-tolylbiguanide, several runs were carried out on a pilot plant scale (50 kg.). The results are consistent with the bench scale procedure and yields of over 90% were realised. The product meets the specifications and about 600 kg. of Sopanox was prepared and sold to an interested party. The process was finalized and is being released for commercial exploitation.

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

The preparation of dyes for synthetic fibres, based on the work mentioned in the earlier report was continued. The dyes so far prepared have been examined by thin layer chromatographic technique and the purified samples were isolated and analysed. The testing of these dyes in regard to their affinity studies and fastness properties (light, sublimation, washing, gas-fading etc.) was carried out in collaboration with the textile chemistry division of the Department of Chemical Technology, University of Bombay, Bombay. This aspect is now complete and the study has revealed certain interesting features. The invention is being finalized for a patent.

The accumulation of spectral data and other physical properties of the purified dyes is in progress.

15. *Triethyl phosphate :* (ATT-24/66)

Triethyl phosphate is used as a catalyst in the manufacture of ketene from acetic acid. At present most of the requirements (50 TPA) are met by imports, valued Rs. 6 lakhs. Triethyl phosphate is also used by the plastic industry as a plasticizer.

The laboratory scale preparation of triethyl phosphate in 95% yields by the action of phosphorous oxychloride on sodium ethoxide in absolute ethanol was reported earlier. The project is being scaled up on a pilot plant for collecting data on larger runs. The construction of the pilot plant assembly is complete and larger runs are being tried. The pilot plant runs are in progress and the process will be finalized soon and made available to interested parties.

16. *Reactive dyes :* (ATT-25/65)

The standardization of the technical preparations of several reactive dyes, covering the complete range of colours has been completed. Red, bluish red, violet and orange colours were mentioned in the earlier report and the range was extended to include yellow and a turquoise blue dye prepared from copper phthalocyanine.

17. *Tri (nonylphenyl) phosphite (Polygard) :* (ATT-71/67)

Tri (nonylphenyl) phosphite (TNPP) has been recently introduced in U.S.A. and is sold under the trade name 'Polygard'. It is a superior stabilizer for GRS polymer and white rubber. It is preferred over aryl phosphites as it is non-discolouring and imparts less odour to the finished polymer. It is more resistant to hydrolysis and hence could be added to latex as an aqueous emulsion.

The demand of one party alone in the country is about 70 TPA valued approximately Rs. 10.5 lakhs. At present this is entirely imported and the demand is likely to go up if it is indigenously produced.

Several laboratory runs were carried out for standardizing the technical preparation. Large scale batches (25 kg.) will be prepared before the process is offered to industry.

18. *Potassium ethyl xanthate andpotassium amyl xanthate* : (ATT-70/67)

These two chemicals are used in the flotation techniques of ore-dressing and are imported into the country in large quantities. The processes for the preparation of both the xanthates were standardized on a laboratory scale. The prepared material meets the specifications and large scale experiments are planned. The processes are being finalized for commercial exploitation.

19. *Vanillin* : (ATT-106/68)

The work on the technical synthesis of vanillin was continued further after the sponsored scheme was abandoned. The preparation of guaiacol from *o*-anisidine was carried out on 50 g. batches in the preliminary runs reported earlier. This process was scaled up to 500 g. scale and several runs were carried out. A continuous method for the extraction of guaiacol from the steam distillate as well as purification of the crude guaiacol was worked out and yields around 72% were consistently realized. The second stage of conversion of guaiacol to vanillin however, gave lower yields than expected.

20. *Hydroxyethyl starch* : (AB-60/68)

Since blood or plasma is difficult to obtain and preserve on a large scale, production of plasma substitutes for the treatment of shock has been extensively studied in many countries. Many fluids based on gelatin, dextraven, polyvinyl pyrolidone etc. are being used; however, the only substance in wide use is dextran. Dextran also has its own limitations particularly in its storage properties. As a result of a search for a new substitute for dextran, hydroxyethyl starch (HES) has been recently introduced in the U.S.A.

According to a process reported to be followed in U.S.A., HES is prepared by condensing amylopectin and ethylene oxide. It is also reported that HES is extensively used in the textile and paper industry. Inquiries have therefore been initiated to find its market potential in the country in different industries.

A few experiments were conducted to prepare HES from maize starch and ethylene oxide in presence of alkali. The products were tested for their solubility, viscosity and adhesive properties. Further work on the analyses of these HES is in progress.

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

This work has been undertaken with a view to study the production of glucose by saccharification of cellulosic agricultural wastes.

By the action of hydrochloric acid, about 35% of native cellulose could be converted to D-glucose, while 55% conversion was obtained in case of rayon grade pulp prepared from groundnut shells. In the course of this reaction the unreacted cellulose is recovered as a fine powder.

Cellulose powder finds considerable use as a chromatographic adsorbent and also as a filler in some plastic products. 800 TPA of cellulose powder is being imported for use in the plastic industry.

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

Certain glycosides and thioglycosides derived from D-galactose and D-fucose are important requirements for " Lac-opron " and other studies in genetics. Other glycosides and some synthetic carbohydrates are also in demand for research purposes.

Most of these glycosides are costly and methods of preparation of many of them have not been reported so far.

A number of these glycosides and thioglycosides have been prepared and exported to U.S.A. and supplied to some institutes in India.

Another synthetic carbohydrate 3-*o*-methyl D-glucopyranose has been prepared and supplied.

A method developed in this Laboratory for the preparation of aryl-α-glycosides and thioglycosides (Indian Patent 109489) has been utilized for the preparation of all of the aryl-α-glycosides.

The following ten different glycosides as well as 3-*o*-methyl-D-glucopyranose were prepared and supplied during the period of this report:

1. *o*-Nitrophenyl β-D-thiofucopyranoside
2. *o*-Nitrophenyl β-D-thiogalactopyranoside
3. Phenyl α-D-thiogalactopyranoside
4. Phenyl β-D-thiogalactopyranoside

5. *o*-Nitrophenyl α-D-thiogalactopyranoside
6. *o*-Nitrophenyl β-D-galactopyranoside
7. Phenyl α-D-galactopyranoside
8. Phenyl β-D-galactopyranoside
9. Phenyl α-D-glucopyranoside
10. Phenyl β-D-glucopyranoside

23. *Substitute for gum Arabic :* (ATT-107/66)

This work was undertaken at the instance of Indian Posts and Telegraphs Board for developing a substitute for the imported gum Arabic. Some samples of modified indigenous gums prepared in the course of this work have been approved by the P. & T. Board.

Gum Arabic has numerous uses in dyeing and printing, food and pharmaceuticals, paper, match-sticks, adhesives and other industries. Imports of gum Arabic during 1966-67 were 3260 tonnes. The landed cost is Rs. 6/kg. and the market price is around Rs. 12/kg.

In order to evaluate the commercial feasibility of the process, a market survey for the availability of gum Ghati, Karaya and Jeol, was conducted. It has been gathered that about 15,000 tonnes of gum Karaya and others valued approximately Rs. 3 crores are exported. The prices vary from Rs. 2000/- to Rs. 4000/tonne.

Large scale trials of the modified process will be undertaken for further evaluation of the product.

24. *Cellulose caprate :* (ATT-108/66)

Cellulose caprate of certain specifications is the main ingredient of an optical cement composition of outstanding value. This cement is imported at present. The process for the preparation of cellulose caprate of required specifications has been standardized on a laboratory scale.

A quantity of this material has been prepared and supplied to a local optical instruments manufacturer for trials. A sample of this material has also been supplied to Defence Research Laboratory, Kanpur, at their request.

Steps are being taken to scale up the process and also to prepare the actual cement by incorporation of certain plasticizers in it.

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

In view of the development of more economical processes for the synthesis of pyridoxine, abroad, the commercial feasibility of the process already worked out in this laboratory, has become doubtful. New methods of synthesis which have appeared in the literature since 1960 were critically reviewed and laboratory investigations on a commercially feasible process have been initiated.

26. *Diethyl-m-toluamide :* (ATT-18/65)

The compound is known to be useful insect repellent, and is not produced in the country. In view of the non-availability of pure *m*-xylene, commercial xylene was oxidized in 5 kg. lots in a batch process using oxygen and catalysts for conversion to mixed toluic acids. This acid mixture was next condensed in a continuous reactor with diethylamine to give a product containing approximately 70% diethyl-*m*-toluamide. Several litres of this material were supplied to AFMC Field Laboratory for field trials. The product has been found to be satisfactory.

27. *para-menthane hydroperoxide :* (ATT-109/67)

p-Menthane hydroperoxide (PMHP) is used as a low temperature polymerization catalyst for the manufacture of styrene butadiene copolymers.

Present requirement of this chemical of one party alone is about 40 TPA valued Rs. 6.3 lakhs. The demand is likely to increase up to 60-70 TPA valued Rs. 10-11 lakhs.

Starting from dipentene a process for the technical preparation of *p*-menthane hydroperoxide has been standardized on 5 kg. batch scale. The product has been tested by the consumer and found satisfactory. The process is being offered to the interested party.

Meanwhile, some work on the preparation of *p*-menthane hydroperoxide in a continuous reactor has been carried out.

28. *Colchicine :* (AB-19/67) (ATT-68/68)

Colchicine is valuable both in pharmacy and plant breeding. Techno-economic survey has shown that the current indigenous demand is approximately 2 kg. valued more than Rs. 70,000/-, and by 1970-71 the demand is likely to be double. Moreover, since colchicine is in short supply in the world market, its' export potential would be good.

The currently known indigenous sources of this alkaloid have been examined and a suitable method for the extraction of colchicine is being standardized.

In collaboration with the Forest Utilization Officer, Poona, steps have been taken to cultivate the required plant.

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

This chemical is used to stimulate cell proliferation for ulcers, non-healing wounds, fistulas etc. This is also largely used in the cosmetic industries and is not being prepared in the country.

Starting from dichloroacetic acid and urea, allantoin has been prepared in an yield of about 40% on the basis of dichloroacetic acid, which is much higher than reported in literature. Further work is in progress.

30. *Synthetic experiments on berberine alkaloids* : (B-8.30/68)

Berberine hydrochloride is being extensively used particularly in Japan, in the treatment of certain kidney disorders which are caused by excess alcohol consumption. Investigations have been undertaken to work out a simple synthesis of the compound and its analogues.

In the course of this work a new approach for the synthesis of protoberberine alkaloids has been successfully developed starting from 3-phenylisoquinoline.

31. *Ethylene brassylate* : (ATT-26/67)

Ethylene brassylate is a perfumery material having musk-like odour and is used widely in perfumes. It is not manufactured in India.

Starting from ethyl erucate (from mustard oil) through brassylic acid, a laboratory scale preparation of ethylene brassylate has been standardized. The product is being evaluated, and the project is concluded.

32. *para-nitrophenol* : (ATT-73/67)

p-Nitrophenol is required for the production of pesticide 'parathion' and is at present imported. The estimated demand of *p*-nitrophenol used for 'parathion' is of the order of 300 TPA, furthermore it is likely to increase to 2000 TPA. Raw material, *p*-nitrochlorobenzene, required for the synthesis of *p*-nitrophenol will be available from Hindustan Organic Chemicals, Rasayani.

Laboratory scale preparation of *p*-nitrophenol from *p*-nitrochlorobenzene has been standardized. Scaling up work is in progress.

33. *Acetyl sulphanilyl chloride* : (ATT-72/67)

ASC, an important intermediate in sulfa drug manufacture, is prepared by the chlorosulphonation of acetanilide using an excess of chlorosulphonic acid. This product is used immediately in the next step as it cannot be stored for long periods; also by the present manufacturing process, there are, technical problems in getting a dry product that can be stored without deterioration.

A process has been standardized in the laboratory whereby a technical grade dry ASC of 97-98% assay could be produced in greater than 70% yields. Stability tests, however, indicate that the product even on careful storage deteriorates progressively with time, the assay after 1 month's storage being about 86%.

The sulfuric acid mother liquor in the above process can be obtained in much higher concentration than in current manufacturing methods, making it possible to utilize this waste acid, for example, in the superphosphate industry. Sulfanilic acid can also be recovered from this waste acid.

34. *Extraction of inulin from costus roots and conversion of inulin* (ex. costus roots) *to fructose :* (ATT-29/67)

Fructose is a sugar tolerated by diabetic patients and is employed in the form of injections for cases of stress, due to surgery and starvation. The fructose requirement of India is now entirely met by imports.

Although it was known earlier that costus roots contain the fructose polymer, inulin, the roots were never suggested as a commercial source for the production of fructose. It has been found now that inulin can be extracted from costus roots, exhausted of the essential oil, to the extent of 25% on the weight of the roots. Conditions were standardized for the preparation of inulin from the exhausted costus roots. About 8 kg. of inulin was prepared and its hydrolytic conversion to fructose on 500 g. scale has been carried out. Fructose syrup and crystalline fructose were prepared from the hydrolysate. These processes have been covered by two Indian Patents (108413 and 108414).

150 g. of crystalline fructose has been prepared from inulin and supplied to an interested party for evaluation.

35. *Development of stationary liquid phases and solid support for GLC instruments :* (AB-33/63)

Investigations on Indian firebrick : Because of non-availability of imported GLC supports such as chromosorbs, celite, sterchamol etc., locally available material was investigated as support and its proper evaluation was undertaken.

A systematic comparison between imported celite - 545, supporting material and Indian firebrick powder has been carried out. One of the polyesters, prepared in the laboratory was added on firebrick powder at various percentages and each column was run under identical conditions to find its efficiency. Various efficiency measures (such as values of S,Q,R, HETP etc.) were carefully calculated and compared with the values on celite 545 columns. It was found that our laboratory-made support is a good substitute for imported material. Further improvements will be carried out to increase its efficiency.

Development of new polyesters : Several new polyesters containing unsaturation have been prepared, tested for their efficiency and found useful for VPC analysis of oxygenated compounds.

36. *Transformation products of citral :* (AB-32/66)

India produces lemongrass oil in large quantities mostly in Kerala state. The export of lemongrass oil has been steadily declining due to the production of citral from α-pinene in Europe and U.S.A. The situation warrants more outlets for the economic utilization of lemongrass oil (chief constituent-citral) from indigenous natural source.

Citral has been converted to citral epoxide in high yields. A new one-step method has been developed for the conversion of citral to citronellol in good yields.

Hydrogenation of citral in the presence of Raney nickel catalyst has been studied to establish optimum conditions for the preparation of *dl*-citronellal. Part of this work has been undertaken as a sponsored project.

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

The annual demand of theophylline and its derivatives is estimated at 20-25 TPA, valued Rs. 10 lakhs. At present theophylline and its derivatives are imported.

Exploratory work on the synthesis of theophylline based on 1,3-dimethylurea has been started.

38. 19-*Norsteroids and other modified steroids :* (ATT-30/67)

19-Norsteroids of anabolic and antifertility activity are gaining considerable importance.

Optimum conditions for the preparation of Δ^4-tigogenone involving the Oppenauer oxidation of diosgenin have been established. Conversion of

Δ^4-tigogenone to the 2,6-dibromo compound and subsequent dehydrobromination according to a literature method furnished the $\Delta^{1,4,6}$-trienone in rather low yields. Treatment of 5α, 6β-dibromocholestanol and 5α, 6β-dibromotigogenin with a strongly basic reagent did not furnish the expected conjugated diene, but resulted in debromination. A convenient procedure for the reduction of cholesterol to cholestanol has been developed.

The degradation of bile acid side chain by some new routes is being explored. The action of lead tetraacetate on 24-hydroxycholane has been studied and the resulting oxide has been characterized.

39. *Chamazulene from dehydrocostus lactone :* (AB-30/67)

A large amount of crystalline lactones separates out during the extraction of costus root oil. The object of the project is to find commercial utilization of these lactones since their derivatives are likely to find use in medicine and cosmetics.

Chamazulene and other azulenes possess anti-phlogistic and other medicinal properties.

A process has been developed for obtaining chamazulene from dehydrocostus lactone, *via* its dihydroderivative, in 20% yield. This involves heating of the dihydroderivative with diethylene glycol and alkali at high temperatures.

When the 12-methoxy derivative is subjected to the same treatment a mixture of azulenes is obtained in 10 to 15 % yield. This contains about 75 % chamazulene.

A sample of chamazulene has been supplied to a party for evaluation.

40. *Ion exchange resins :*

40.1 *Styrene-DVB base cation exchange resin :* (ATT-33.2/62). At the request of one of the licensees of this process, experiments were conducted to sulphonate styrene-DVB copolymer, without the prior swelling as originally recommended. It was found that resin of required characteristics could be prepared using silver sulphate as catalyst, without prior swelling of the copolymer beads. In view of the high cost of silver sulphate, its application in large scale production is however, uneconomical.

A procedure for the sulphonation of the imported copolymer was also worked out. A detailed demonstration of the NCL (improved) process for the preparation of the copolymer, its sulphonation and washing to yield a good quality cation exchange resin, was given to one of the licensees of the process. The party, satisfied with the results, is now taking steps to establish the manufacture of the resin by the improved process.

40.2 *Cation exchange resin from phenol-formaldehyde resin scrap :* (ATT 33.4/67). During the manufacture and moulding of phenolics some quantity of the scrap accumulates. The sulphonation of phenol-formaldehyde matrix for preparing cation exchange resins has been studied. The phenolic moulding powder usually contains about 50% of wood powder as filler. By sulphonation of the scrap under suitable conditions sulphonic type cation exchange resin has been prepared. The resin has a low capacity, but can be used in water softening and removal of fluorides from water. However, due to its low capcity, the exchanger is not likely to be economical, so further work on the project has been discontinued.

40.3 *Acrylic base cation exchange resin :* (ATT-33.1/66). Further experiments were carried out in standardizing conditions for the suspension copolymerization of methacrylic acid and divinyl benzene to obtain this weakly acidic resin in spherical shape of desired volume capacity. The prime objective of the work was to obtain free-flowing, nonsticky, spherical beads of the required volume capacity. Investigation on the performance of the product in columns has shown that generally both the volume and breakthrough capacities are low. The low volume capacity is due to the macroporous nature of the resin caused by the dissolution of water in the monomer medium. The low breakthrough capacity is due to the stickiness of the product leading to choking and channelling in the columns.

Saturation of the suspending medium with inorganic salts was tried to prevent the dissolution of monomer in aqueous medium and vice versa. The use of various suspending agents under varying conditions of stirring was tried to get a stable suspension leading to spherical particles. The use of partially polymerized methacrylic acid was also tried to get a tough and hard resin. It has been, however, possible to obtain beads (not completely spherical) of fairly high volume capacity by using saturated salt solution as the suspending medium and polymethacrylic acid as the suspension stabiliser under slightly acidic conditions. Further improvements of the suspension process to get completely spherical beads of desired volume capacity are under investigation.

41. *Polystyrene foams :* (ATT-34/60)

Polystyrene foams are mainly used in low temperature insulation and their use in packaging is slowly growing in the country. At present one firm is manufacturing the product using imported know-how. Although there are no imports of similar products, the demand in the country in the near future is expected to be of the order of 2,000 TPA valued at about Rs. 2 crores.

Following previous work on a 2 kg. batch scale, trials were taken with a 20 gallon kettle producing about 15 kg. of the expandable beads per batch. Several difficulties, particularly in regard to maintenance of pressure and accurate temperature control throughout the reaction, have been overcome. Some modifications in the design of stirrer blades and conditions of stirring during the polymerization have been made. The use of an indigenously available suspending agent in the polymerization reaction has been found to be not only economical but very effective in reducing chances of agglomeration, thus yielding glassy transparent beads similar to those manufactured elsewhere. Foamed sheets (15 cm. × 15 cm. × 2.5 cm. and 76 cm. × 38 cm. × 10 cm.) were moulded from prefoamed beads. Further experiments to get beads of the required size and lower densities of the mouled sheets are being continued. A mould with improved design (100 cm. × 50 cm. × 10 cm.) and a device for slicing these sheets have been designed and are under fabrication.

42. *Polyurethanes :*

42.1 *Coating for nylon fabric :* (ATT-47/64). Shellac based coatings for nylon fabric have been prepared on small scale and have been found suitable. A demonstration of this process is to be given to a representative of SASMIRA, Bombay.

42.2 *Typewriter rollers :* (ATT-38/65). Typewriter roller tubes were prepared by extrusion. Thus it is now possible to make tubes on a production scale by this technique. A report from a typewriter manufacturer on a tube made from an improved formulation is awaited.

42.3 *Urethane rubber :* (AB-37/64). Process of preparing polyesters needed for making urethane rubber was standardized. A new process of vulcanization of these rubbers has been established.

42.4 *Composite propellant :* (ATT-37/63). Samples of the binder supplied to the Defence department were found suitable for about 72% fuel loading. The loading is to be increased to 80% by suitable change in the formulation.

42.5 *Material for artificial limbs :* (ATT-88/67). Imported samples of polyester-polyisocyanates are awaited. Some rigid foams using shellac polyester have been made. It is felt that a shellac castor oil formulation may be suitable for this purpose.

42.6 *Leather coatings :* (ATT-103/68). A sample of the coating was supplied to the interested party. The coating was found suitable for its application on footwear. The party is interested in exploitation of the process.

43. *Surface Coatings :*

43.1 *Styrenated alkyds :* (ATT-97/67). Styrenated alkyds are known to be superior to ordinary alkyds in their various applications. Following laboratory experiments and test reports, the preparation of a styrenated alkyd was scaled up to a 20 litre/batch. Evaluation of the product so obtained showed good film forming properties but had a poor pot life (which had not been observed in laboratory experiments of even 5 litre/batch), besides gelling of the product during preparation in a few cases. Gelling could be attributed to inadequate temperature control in the reaction. Efforts are, however, being made to find suitable remedies before the process is released to industry.

43.2 *Linseeed oil emulsion :* (ATT-49/66). This study is aimed at the development of a low cost water thinnable linseed oil based emulsion for use in place of plastic emulsion paints.

It has been found that linseed oil, polymerized with the use of SO_2 and CO_2, gives better emulsions than the vacuum-heated polymerized oil, though the finished product from the former cannot be pigmented with zinc oxide. Using different emulsifying agents, satisfactory emulsions have been prepared with SO_2-CO_2 polymerized linseed oil and later pigmented with TiO_2. These water thinnable emulsion paints have been applied on masonry surfaces and they are comparable with plastic emulsion paints available in the market. Larger batches of these compositions are being prepared for tests by outsides parties.

Techno-economic data on the product are also being collected.

43.3 *Epoxy resin coating :* (ATT-98/68). Novolac type phenolic resin, using different proportions of phenol and formaldehyde was prepared and reacted with epichlorohydrin in presence of alkaline catalysts to obtain epoxy resins. Chemical resistance of air dried and stoved films prepared from these resins is comparable with those obtained from Bisphenol-A-based commercial epoxy resins, besides showing better heat resistance. They can be applied to both wooden and metal surfaces.

Large quantities of the resin will be prepared for trials by outside parties.

44. *Adhesives :*

44.1 *Cement for diamond setting :* (ATT-40.3/66). The Indian diamond industry has been hit by the non-availability of a special type of imported cement used for setting diamonds for polishing. A systematic study of the chemical composition of the resin used in the imported cement established it to be a linear mixed polyester of terephthalic acid. The two glycols used therein have been identified (one of these had to be specially synthesized) and a few formulations of the cement were prepared therefrom. These were found to be suitable for use in large size diamonds, but the industry also wants a cement with higher softening temperature that could be used in the setting of small size dimonds. A few more samples of the polyester resin using different proportions of the glycols are being synthesized for use in preparing the cement with higher softening point. These will be sent for trials to the interested party.

44.2 *Adhesives for staple pins :* (ATT-40.1/66). Based on the results of trials, some modifications in the composition of the adhesive were made. Further satisfactory trial reports of this composition have been received from an outside party. A bulk sample was subsequently prepared for extensive trials on automatic machines and this has been found to be generally acceptable. The process is now ready for release to industry.

44.3 *Self-sticking composition for paper labels :* (ATT-40.4/66). Following the satisfactory report from the Ministry of Home Affairs, further 5 lbs. sample was prepared and supplied to the Ministry.

44.4 *Rubber base adhesives :* (ATT-42/66). Work on adhesives needed by HAL, Bangalore, is being continued. Many new formulations were prepared and their properties studied.

45. *Rubber and allied products :*

45.1 *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. About 500 tonnes of this rubber valued at about Rs. 50 lakhs are annually imported; with indigenous availability, its annual consumption could be expected to rise to about two to three thousand tonnes valued at Rs. 2-3 crores.

Laboratory work for the preparation of medium nitrile content rubber has been carried out. Copolymerizations have been carried out in 500 ml. glass bottles at 5°. Initial difficulties in the purification and handling of butadiene and in standardization of the method of estimation of nitrile content of the copolymer have been overcome. Systematic experiments have been carried out on the effect of comonomer ratio in the feed, catalyst and soap concentration on the copolymer composition and the conversion. It has been possible to fix initial monomer ratio of acrylonitrile to butadiene in the monomer feed so as to obtain the resulting copolymer with the required 34% nitrile content over a conversion range of 20 to 60%. Above 60% conversion, there is a sharp drop in the nitrile content of the resulting copolymer. It is also observed that with this feed ratio, the initial charge of catalyst and activator leads to a maximum conversion of 25% when alkali washed butadiene is used and to 35% when freshly distilled butadiene is used. Conversions of the order of 60% and above in 8 hrs. have been achieved by a two-step addition of the activator. Preliminary trials of compounding and testing of the rubber thus obtained have shown promising results. Short stopping the reaction at 60% conversion, coagulation of the latex and further processing of the copolymer have to be standardized, following which the polymerization studies will be scaled up.

45.2 *Thiokol rubber :* (ATT-89/67). Attempts have been made to prepare liquid thikol on a small scale. A process to vulcanize these into solid rubber is under examination.

45.3 *Rubberised cork sheet :* (ATT-99/66). A process for the preparation of rubberised cork sheet was developed and released to a party. Another party approached with a similar problem, which called for some modifications of the earlier technique as well as the formulation. Trial samples have been approved by the party to whom the process is being released.

45.4 *Utilization of coir pith :* (ATT-39/66). Four sample gaskets measuring 460 mm x 460 mm x 3 mm have been supplied to an interested party for evaluation.

45.5 *Latex foam backed coir :* (ATT-100/66). The object of this work is to develop a suitable recipe and technique for the preparation of latex foam and its subsequent application to the coir fibre for improving the cushioning properties. It has been taken up at the request of an outside party. Preliminary experiments have been carried out to prepare latex foam with increased setting time and to study its behaviour with coir fibre.

45.6 *Rubber reclaiming agents :* (ATT-51/66). The process has been worked out on large seale and is being released.

45.7 *Blowing agent :* (ATT-50/63). A process for making blowing agent with the proper stabilization system was fully worked out. The process is being released to a party.

46. *Miscellaneous polymeric products :*

46.1 *Studies in CNSL* : (ATT-50/63), (AB-38/66). Work on the preparation of rubber accelerators using THA is in progress. Some work is being done on epoxy base component from CNSL as stabilizer for PVC.

46.2 *Upgrading of rosin :* (ATT-101/67). This work was taken up at the request of a rosin manufacturer. It has been established by experiments that good quality turpentine and rosin can be distilled from waste exudes directly with minimum loss. A final report on the work has been sent to the party with samples of the finished products. The party is taking steps to exploit these findings.

46.3 *Bus bar compound :* (ATT-102/68). At the request of M/s Heavy Electricals, Bhopal, an investigation on the preparation of a substitute for the imported bus bar compound was taken up. A few formulations based on indigenous raw materials were prepared and sent for trial to the party. Barring a few shortcomings, one of the formulations was found to be generally comparable to the imported product. An improved sample was subsequently prepared and has been reported as satisfactory by the party. Large quantities of this sample are being prepared for trials by several other interested parties in the country. Technoeconomic data on the product are being collected.

47. *Foundry chemicals :*

Foundry chemicals are important in the economy of the country. Indian locomotives, wagons, machine tools and other engineering goods are in increasing demand even in foreign countries. At present the cost of some of these chemicals is an obstacle in the greater production of high precision castings, for which there is a good export market. A proper price structure of foundry chemicals is also basic to the development of many other industries in the country.

47.1 *Shell moulding resin :* (ATT-54.1/66). Shell moulding, first developed in Germany after the World War II, has been widely accepted because of its manifold advantages over the conventional technique. The process utilizes a specially made phenol-formaldhyde resin. The object of the present work is to produce this resin from entirely indigenous raw materials at a price substantially lower than the present price of Rs. 8/- to Rs.10/- per kg. Compositions based on CNSL and urea-formaldehyde resins utilizing certain industrial and agricultural wastes and novel catalyst systems have been made and tested for their curing, baking and mould release properties by making shell patterns in the laboratory. One composition, which was found suitable in laboratory trials, was prepared on 5 kg. scale and sent for evaluation. On the basis of the evaluation report, more samples will be prepared for trials.

47.2 *'Sinol' core binder :* (ATT-54.2/63). 'Sinol' type core binder is used almost exclusively for steel foundry. It gives high tensile strength and non-smoking characteristics with good surface finish and dimensional accuracy. The formulation of the binder is based on waste sulphite liquor and triethanolamine from which it derives its name. Not being made in India, its requirement has so far been met by imports. A composition based on the Indian magnesium-based sulphite liquor, in place of the calcium-based sulphite liquor used in Sinol has been developed. Efforts are being made to produce it more economically and saleable at a competitive price.

47.3 *Dry core binder :* (ATT-54.3/65). This binder, very popular in small foundries, is based on dextrin and some inorganic materials. The object of the present work is to avoid excessive smoke formation from its use during the casting operation and also to produce it more economically. Compositions based on modified sulphite liquor and rosin were worked out and tested for their green strength and other physical and baking characteristics. A sample has been sent for evaluation. On the basis of the report, the product will be suitably modified for more extensive trials.

47.4 *Starch phosphate :* (ATT-54.4/64). This well-known product finds considerable application in the canning of foods, in adhesives, ore refining and foundry work. Compositions were worked out using indigenous tapioca starch and are evaluated for their phosphorus contents and other characteristics, such as the proportion of soluble and insoluble phosphates. Samples made were also tested for their performance in the foundry and elswhere.

47.5 *Double boiled linseed oil substitute :* (ATT-54.5/67). Double boiled linseed oil is usd as a conventional sand binder in foundry industry. A composition which can be used as its cheap substitute was developed and found satisfactory when used along with dextrin and starch. On the report that the compound does not give good results when used along with tamarind kernel powder (TKP), experiments were undertaken to modify the composition accordingly, so as to give good performance with TKP. A sample of this modified composition is now being evaluated.

48. *Low temperature fluxes :* (ATT-85/68)

Low temperature fluxes are used for soldering electronic parts. These fluxes are not at present made in the country and are imported on a considerable scale. They are marketted in the form of coated solder wires. Samples of fluxes made from entirely indigenous raw materials have been prepared and have been sent to industry for examining consumer acceptability.

49. *Methylamines :* (ATT-57/66) (PP-9/68)

Methylamines are the basic chemicals for the production of a number of important agricultural and industrial chemicals. Being the starting materials for the production of a number of pesticides, fungicides and herbicides, they have assumed added importance in the country's programme of agricultural production. Currently, about 1500 TPA of methylamines (40%) valued at Rs. 44 lakhs are imported. The demand for 1970-71 is estimated to be 3000 TPA (100%) of dimethylamine and another 1000 TPA of monomethylamine. This will be mainly required for the production of ' Sevin ' type agrochemicals.

Several runs have been carried out on a laboratory scale to explore process conditions for the production of methylamines such that the selectivity would be maximum for either monomethylamine or dimethylamine. Since it will be necessary to evaluate the process conditions on a pilot plant, this work is being continued as a pilot plant project for which a separate allocation has been requested.

50. *Ethylenediamine :* (ATT-58/66) (PP-10/68)

Ethylenediamine is an important starting material for the manufacture of industrial organic chemicals such as EDTA (ethylenediaminetetra-acetic acid), EDNA (ethylenedinitramine) and EDT (ethylenediaminetartrate). It is also used in the manufacture of organic fungicides, pesticides, rubber chemicals, etc.

At present the chemical is not produced in the country. Imports for 1966-67 were 53 tonnes valued at Rs. 3 lakhs. The demand for pesticide manufacture alone is estimated around 550 TPA and the total projected demand for 1970-71 would be around 1200 tonnes valued at Rs. 90 lakhs.

A process for producing ethylenediamine from ethylene dichloride and ammonia has been standardized by statistical methods on a laboratory scale and conditions have been optimized. Since it will be necessary to set up a pilot plant and evaluate the process, this work is being continued as a pilot plant project for which a separate allocation has been requested.

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

Phenacetin is a widely used chemical in the pharmaceutical industry. About 188 tonnes valued at Rs. 18.66 lakhs were imported during 1966-67.

Acetylation of *p*-phenetidine was carried out in high yields by an improved process. A number of runs on 40 kg./batch scale have been carried out and engineering and process data have been collected.

The process has been scaled up to 100 kg/ batch and one tonne of the finished product has been prepared for M/s IDPL, Hyderabad, using raw materials supplied by them. In the course of these runs additional engineering data have been collected for scale up.

52. *Vitamin C and Sorbitol :* (ATT-55/66)

The process for the production of vitamin C starting from glucose has been taken up by M/s Hindustan Antibiotics Ltd., Pimpri, based on pilot plant trials both at NCL and HAL. HAL have been licensed for the manufacture of vitamin C (125 TPA) and are taking further steps to implement the project as early as possible.

To cut down the cost of production of sorbitol, an intermediate in the process, a process for the hydrogenation of invert sugar (instead of glucose which gives only sorbitol) with subsequent separation of the two products sorbitol and mannitol, has also been worked out. For optimizing the yields and obtaining high purity of the two products, analytical estimation of the two in the presence of each other was found necessary. Being isomers, they presented considerable difficulty and various methods were tried. Paper chromatographic separation of the acetates of mannitol and sorbitol did not give good results; GLC of the acetates indicated that they could be separated quantitatively; a method based on UV absorption was tried to estimate mannitol, sorbitol and a mixture of mannitol and sorbitol. Finally a TLC method was found to give fairly satisfactory results and this is now being standardized.

53. 2,4-*Dinitromonomethylaniline :* (ATT-55/66)

Tetryl is at present manufactured by the simultaneous oxidation and nitration of dimethylaniline. Since the preparation is hazardous, it has been proposed to prepare it by the nitration of 2,4-dinitromonomethylaniline.

Conditions for the preparation of 2,4-dinitromonomethylaniline from the 2,4-dinitrochlorobenzene and methylamine have been standardized.

About 200 kg. of the material were prepared in lots of up to 50 kg./batch. The product has been tested and found satisfactory by ERDL, Pashan, Poona. 10 kg. of the material has been supplied to H.E. Factory, Kirkee for developing a continuous process for the preparation of tetryl. Further quantities will be supplied to them as and when required.

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

Revised cost estimates based on the recent pilot plant trials were submitted to a party interested in the process. Details such as material balance flow sheet, time schedule, energy and power balance for individual operations for a plant producing 1050 kg. of ethyl acetoacetate/day have been submitted.

Experimental work on separating ethyl acetate and ethanol from their binary mixture obtained in the process is in progress.

55. *Methylol stearamide :* (ATT-104/67)

The work on the preparation of methylol stearamide on a pilot plant scale was concluded after producing the required quantity of the final product of the desired specifications.

56. *Chlorination of sewage methane :* (ATT-92/67)

An agreement is being signed with a Bombay firm to further develop the carbon tetrachloride process of the NCL on a semicommercial scale at a site allotted by the Bombay Municipal Corporation near Dadar Sewage Purification Works. Drawings of the proposed fluidized bed reactor with the ancillary process set-up have been supplied to the firm and the plant is being installed. After the pilot plant for carbon tetrachloride goes into regular trials, conditions for the simultaneous production of perchloroethylene and carbon tetrachloride by the chlorination of methane will be investigated.

57. *Bacterial diastase :* (ATT-32/66)

Assistance was rendered to the firm, to which the process had been leased, in carrying out fermentations at the factory. A contaminant which interfered with the fermentation was isolated and its effect on the diastase producing strain was investigated. In spite of lack of sterility in the fermentors due to leaks, contamination was reduced by a modified procedure and a few fermentations in the 5000-litre fermentor were carried out with good yields of the enzyme. Several fermentations were also carried out in the laboratory to supply broth for studies on filtration and drying of the product.

58. *Preparation of biochemicals :* (ATT-96/69)

50 gms. each of (+)-and (—)-citramalic acid sodium salts and 10 gms of D_5(+)-isocitric lactone have been supplied to a firm in U.S.A. and the Biochemicals Unit of the CSIR, Delhi. The total value of these biochemicals is about Rs. 20,000 of which 18,500 is in US Dollars.

59. *Vapour phase chromatograph :* (ATT-63/67)

Flame ionisation detector : A flame ionisation detector and its associated electronic unit using valves was developed for use with VPC equipment developed earlier. Extensive tests were carried out and the detector was proved to be quite sensitive and extremely stable in operation. This unit is now incorporated in VPC equipment and it is possible to select a detector either for thermal conductivity or for flame ionisation by means of a selector switch.

The technical know-how for VPC along with flame ionisation detector is being released to a Bombay firm.

Preparative VPC : Considerable work was carried out for developing an instrument for preparative VPC. It has been possible to inject samples up to 100 mg. and obtain good separation at low temperature in the case of acetone and toluene. Work is in progress to develop a suitable automatic sample collecting system and high temperature operation.

Capillary column : Work on the technique of coating capillary columns for high resolution gas chromatography is in progress. Satisfactory results have been obtained with short tubings and trials are yet to be carried out for full length columns.

60. *Self-balancing potentiometric servo-recorder :* (ATT-111/67)

In connection with ESR spectrometer programme, work on the development of a suitable recorder was undertaken and a model of the unit is completed. This can also be used with various other equipmets such as gas chromatographs and also in industrial process control. The specifications achieved in this unit are as follows :

1. Max. sensitivity .. 1 mV full scale
2. Response time .. 2.5 seconds or better
3. Pen and ink recording system on 10″ wide strip chart.

These specifications are satisfactory for many applications. This recorder has been used with the gas chromatograph with satisfactory performance and comparable to any of the similar imported equipments.

Work is in progress to ensure the performance of the equipment absolutely reliable, stable and repeatable.

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

This equipment is meant for the quick determination (in 6-8 minutes) of the total solids content in a latex composition. Several experiments were conducted for standardizing the conditions of voltage, current, time of heating weight of the sample etc. using natural rubber latex compositions of known total solids contents. The variation in results between the conventional and the new method was 0.5–2.0 per cent in the samples so far tested. To make the unit portable, the equipment has been assembled on a suitable panel and is ready for use.

□ □ □

RESEARCH PROJECTS

1. THEORETICAL INVESTIGATIONS ON SOLID STATE AND MOLECULAR PHYSICS

Materials in the solid state are finding newer and practical applications owing to their interesting semiconducting, superconducting and magnetic properties. The solid state devices find extensive uses in electronic and communication industries.

A knowledge of the basic interaction processes involving electrons, phonons, spins and external agencies such as photons, etc. is essential before any material is commissioned for device fabrication. With this end in view the following fundamental investigations have been undertaken.

1.1 *State of atoms in the presence of crystal and radiation fields :* (B-1.1/65)

The spin and electronic states of magnetic atoms in the presence of static fields and their interaction with external radiations are being studied.

Earlier it was shown that there is a magnetic field associated with the transverse optical modes of lattice vibrations in ionic crystals. Such fields directly interact with the spins of the magnetic atoms, and new type of spin-phonon interaction terms have been obtained. Further, for magnetically ordered systems, these led to a new magnon-phonon interaction term after appropriate spin-wave transformations. The transverse optical phonons also interact with light and the corresponding phonon-photons interaction terms were formulated. Then a combined effect of the above magnon-phonon and phonon-photon was considered and after the elimination of phonon variables by suitable canonical transformation, new processes involving magnon-photon (light) interactions were derived. The explicit form is given by

$$L_{q,\lambda}\, a_q^{\dagger} \alpha_{q+\lambda} \cdot \beta_{\lambda} + L_{q,\lambda}^{\dagger}\, a_q a_{q+\lambda}^{\dagger} \beta^{\dagger}$$

where Lq, λ is the coupling coefficient and

(a_q^{L}, aq), $(\alpha_{\lambda}^{L}, \gamma_{\lambda})$, $(\beta_{\lambda}^{L} \beta_{\lambda})$ are the creation, annihilation operators for the photons and the branches of magnons respectively for the case of a simple antiferromagnet (e. g. MnF_2, FeF_2 etc.).

Based on these interaction processes, the absorption coefficients were calculated. This gave a singularity at the frequency $\omega=2(\omega_A+\omega_e)$, ω_A and ω_e being anisotropy and exchange frequencies. This is in agreement with the available experimental results.

1.2 *Electronic structure of atoms and molecules* : (B-1.2/64)

Electronic and optical properties of atoms and molecules are usually calculated by applying quantum mechanical principles.

Earlier, the electronic properties of some conjugated organic molecules were calculated. In the period under review, the correlation problem in many-electron atoms, considered as a consequence of the divergent nature of the existing Coulomb potential, was taken up. For this, a modified Coulomb potential for interacting point charges was derived. It has the asymptotic form.

$$\frac{e_i e_j}{r_{ij}} \left[1 - \exp(-k_c r_{ij})\right]$$

where e_i and e_j are the charges of the particles which are at a distance r_{ij} apart, and k_c is a characteristic cut-off parameter. Based on this potential the ground state energies of the Helium-like systems (for nuclear charge number $Z=1$ to $Z=6$) were calculated. The wave-function used involved only one variational parameter. The results showed that the bulk of the correlation error is accounted for by this form of the potential. Thus, in a way, this potential is represented by the polarization corrections involved in many-body interactions.

1.3 *Phonon-magnon interactions in magnetically ordered solids :* (B-1.3/61)

Basic interaction mechanism involving elementary excitations in magnetic solids are being formulated and their importance on the transport properties of the system will be evaluated.

Following the successful completion of work involving magnon (all modes) and acoustic phonon, some new interaction mechanisms were developed which involved optical phonon modes. One of the new processes arose from the direct coupling of various spin wave modes with phonons of the transverse optical modes in mangetic insulators.

The dominant part of the interaction is represented in the folowing form

$$H_{int} = -i\left[\sum \phi^{*}_{\sigma t}(b^{\dagger}_{\sigma t}\ \beta_{\sigma} - h.c.) + \sum \Psi_{\sigma t,\lambda}(\beta_{\lambda} + \sigma\, b^{\dagger}_{\sigma t} - h.c.\right]$$

where $\phi_{\sigma t}$ and $\Psi_{\sigma t,\lambda}$ are the coupling coefficients and $b^{+}_{\sigma t}$, α_{λ} and β_{λ} are the phonon creation and magnon annihilation operators of the respective branches. Relaxation frequencies based on these processes lead to temperature-peak effects.

The renormalization of magnon and phonon modes due to magnon phonon interaction was studied by the Green function technique. In the case of ferromagnets, the renormalized magnon energy has the form $E_{\lambda} = D_{o}(1 - bT^{\frac{3}{2}})\lambda^{2}$ which correctly explains the temperature dependence of the coupling constant (i. e. coefficient of λ^{2}). In the antiferromagnet case the degeneracy of two magnon branches is lifted.

1.4 *Exchange interaction in magnetic solids :* (B-1.4/59)

The magnetic moment enhancement in some dilute alloys (e. g. Fe in Pd) was considered in terms of mixing and exchange interaction between host and impurity atoms.

Detailed calculations showed that the magnetic polarization extends upto seventh neighbour from the impurity i. e. over 100 host atoms get ferromagnetically alligned. These results are found in agreement with the neutron scattering data on these systems and the " origin of giant moments" could be explained on this model.

This work has been further extended by taking cognizance of the d-d correlation in the host 4d band. The susceptibility enhancement obtained is in agreement with the result. Study of dynamical spin-spin interactions in such alloys showed that collective modes simulate the optical spin-wave modes rather than the acoustic modes.

1.5 *Interaction involving conduction electrons in magnetic metals and alloys :* (B 1.5/63)

Earlier, the resistance minimum phenomenon in dilute alloys with non-magnetic impurities was studied by taking account of a generalized Coulomb and exchange interaction.

This was extended to an alloy having paramagnetic impurities with more than one unpaired electrons. In this situation there has been always a non-vanishing excitation energy in the s-d exchange and potential scattering processes connecting the ground and intermediate states. Based on these considerations, the thermoelectric power was calculated under various approximations. The results are found to be in good agreement with a large number of alloys.

The problem is concluded.

1.6 *Superconductivity in metals and alloys :* (B-1.6/63)

There has been world-wide search for superconductors with high transition temperatures. These systems are employed for a number of practical applications. Earlier, the effects of pressure, impurity and structure were studied in relation to the transition temperature of superconductors.

Further work has shown that some specific two-body electronic interactions lead to enhancement of the transition temperature, whereas one-body effects of various kinds tend to decrease T_C. The final expression of the transition temperature is represented by the sum of several competing processes.

The possibility of induced superconductivity in some semi-conductors has been investigated and the approach appears to be promising.

1.7 *Mobility in polar semiconductors :* (B-1.7/63)

Earlier, a general theory of mobility in semiconductors involving the concept of multi-band conduction was developed. This explained the behaviour of a large number of compound semiconductors and their solid solutions.

In the period under review, a new mechanism of field dependent mobility was considered which accounted for the static and dynamic polarisation of the ions induced by the electric field. Electron phonon interaction terms have been formulated in which the dependence of the dielectric constant on the deformation in the system by the application of an external electric field has been incorporated. The mobility expression predicted the right trend.

This work has been completed.

1.8 *Ligand field theory :* (B-1.9/68)

Ligand field theory of inorganic complexes in all its mathematical vigour is of great interest for interpreting the absorption spectra, thermodynamic properties and magnetic behaviour of such complexes. The formalism so developed has practical applications in catalysis since there is increasing evidence, of late, that complexes with definite geometrical patterns are formed during chemisorption around active sites and with the adsorbed species.

It is again of importance in a study of the optical properties of doped single crystals and in the theory of lasers. The ligand field theory of octahedral complexes has been worked out thoroughly during the last ten to fifteen years. Complexes with other symmetries such as D_3, and C_{3v} have been discovered only during the last two to three years. A strong field theory of these complexes corresponding to the classic work of Tanabe and Sugano on octahedral complexes is very much in need. This has been just completed here for Ni^{2+} (d^8) complexes and applied successfully to interpret some published absorption spectra.

1.9 *Chalcogenide spinel semiconductors :* (B-1.10/68)

Chalcogenide spinels have come into prominence with the discovery of ferromagnetic $CdCr_2Se_4$. In doped conditions they show high mobility and negative magneto-resistance at low temperatures. They are finding applications in modulators and amplifiers.

In view of this, $CdCr_2Se_4$ in pure and doped states has been prepared and the crystal and electrical properties are being studied.

Some oxidic spinel systems have also been studied in order to assess the contribution to conductivity involving cations at the tetrahedral sites. The systems studied are :

1) $x(Mn^{3+} [Ni^{2+} Mn^{3+}] 0_4) + (1-x) (Mn^{2+} [Cr_2^{3+}] 0_4)$

2) $x(Co^{3+} [Ni^{2+} Co^{3+}] 0_4) + (1-x) (Co^{2+} [Cr_2^{3+}] 0_4)$

3) $x(Fe^{3+} [Ni^{2+} Fe^{3+}] 0_4) + (1-x) (Fe^{2+} [Cr_2^{3+}] 0_4)$

In each system samples with $x = 0.5$ are found to show minimum resistivity with low positive thermoelectric power as compared to the parent compounds.

2. MATERIALS FOR SOLD STATE DEVICES

2.1 *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 integrated circuits and devices such as field effect transistors, negative resistance devices etc.

Earlier, an unusual negative resistance phenomenon in Al/CdS/Al sandwich was observed in this laboratory where the current controlled negative resistance and the voltage controlled negative resistance followed each other in a cycle. A detailed basic study on this system has revealed that at low voltage the conductivity is " space-charge " controlled and at high voltage avalanche multiplication becomes the dominating factor. The dual negative resistance is attributed to the presence of two special types of traps having different capture cross section.

An extension of this study to Al-CdSe (or CdTe)-Au sandwiches has demonstrated interesting switching effects. Initial I-V curve showed a rectifier-like characteristic. On increasing the reverse voltage a breakdown occurred and the structure transforms from rectifying to a bistable state when switching from high conductivity to low conductivity and vice versa took place at appropriate applied voltage. This effect vanished under light.

Further work is in progress to arrive at an explanation for this unusual effect.

2.2 *Laser materials :* (B-2.4/66)

The effect of substituents in rare earth chelates on their fluorescence emission has been studied.

Electron-donor hydroxy or methoxy groups substituted on dibenzoyl methide chelates increased the amount of energy transferred from the triplet state of the ligand to the ion and consequently increased the ionic emission. The reverse effect was observed with electron withdrawing groups.

Combination of aromatic-aliphatic β-diketones such as thenoyl trifluoroacetonate showed a strong ionic emission. This has been attributed to an increased energy transfer from the triplet state to the trivalent ion coupled with higher radiative transition probability between the excited state and the low lying $^7F_0$ levels due to an increased asymmetry about the ion.

2.3 *Photoconducting materials :* (AB-5/62)

Work on the electrical and photoconducting properties of chemically deposited PbS, PbSe, CdS and CdSe films has been continued. The study of the electrical and photoconducting properties of chemically deposited layers has shown that the properties of these layers are similar to those of CdS crystals with regard to the effect of addition of copper. By the use of pulse techniques the trap free current has been plotted and is found to be two orders greater than under d. c. conditions. An investigation of sintered layers of photoconductors is in progress.

3. THIN FILMS

Semiconducting properties of thin films (i) *resistors, thermoelectric power measurements* (ii) *studies on Hall effects and photoelectric properties :* (AB-9/62)

In view of the great technological importance of semiconductors in thin films, a detailed study of their semiconducting properties has been undertaken. The data will be useful in the development of devices such as resistors, capacitors and transistors.

A detailed study has been made on the Hall coefficient, Hall mobility, conductivity, mean free path and carrier concentration of the vacuum deposited films of Tl_2Se, Tl_2Te, HgTe, and HgSe compounds formed at room temperature as well as at higher substrate temperatures. It was found that R_H increased with the increase of film thickness and also with the substrate temperature. Tl_2Se behaved as a semiconductor whilst Tl_2Te showed more or less metalloid characteristics. The energy gap ($\triangle E$) for Tl_2Se was found to vary from 0.33 to 0.40 eV and the thermoelectric power (α) varied between 50-80 μV.

HgTe and HgSe films also showed a similar type of variation for the above semiconducting parameters. Single crystal films were also formed on freshly cleaned mica and the properties were compared with those formed on glass. Higher values were obtained for different parameters in case of single crystal films than the poly-crystalline films formed under more or less the same conditions of evaporation.

Increase of the values of R_H, α μH, 1_O for films deposited at higher substrate temperature is explained on the basis of the decrease in growth defects of the films.

Similar studies are also being carried out on other compounds such as CrSe, CrTe, Ag_2Te, Ag_2Se, GeTe, MnSe, InTe, etc.

4. CRYSTAL AND MOLECULAR STUDIES

4.1 *Crystallography* (B-2.5/59)

Work has been in progress on the precise structure determination of simple organic compounds by X-ray crystallographic method. The purpose of this study is to understand the nature of electronic interaction between the different groups in the molecules from the observed molecular dimensions.

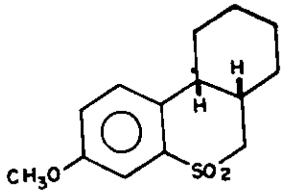
The structure of *m*-aminobenzoic acid hydrochloride has been refined with the help of three dimensional data. It is has been found that the molecules form dimers with short O......OH bonds (2.53Å) the two C–O bonds of the carboxylic group are nearly equal, suggesting that tautomerism of the type O-H......O $\rightleftharpoons$ O........H-O occures.

In order to study the influence of methyl group substitution in para position on the molecular dimensions of benzoic acid, the analysis of *p*-toluic acid was undertaken. The compound crystallized in the triclinic system: space group PI, with two molecules per unit cell of dimensions

$$a = 8.87, \quad b = 7.71, \quad c = 7.57\ \text{Å};$$
$$\alpha = 120^\circ, \quad \beta = 118{\cdot}5^\circ, \quad \gamma = 93.9^\circ.$$

The molecules formed dimers; refinement of three dimensional data is in progress.

The structure analysis of 7-methoxy-9-thia-1,2,3,4,4a,9,10,10a-octahydrophenanthrene sulphone was undertaken in order to find out whether the molecule has the *cis* or *trans* configuration. The compound was shown to have the following structure :



It crystallized in the orthorhombic system, space group Pbnb with eight molecules per cell of dimensions

$$a = 30.63, \quad b = 10.60, \quad c = 7.99\text{Å}$$

The aromatic ring is found planar within experimental error and the puckered ring on the other side of the central ring has *cis* orientation and existed in the chair form.

4.2 *Spectrochemical studies :* (B-5.1/63)

In continuation of the study of dipolar or zwitterionic compounds, the amino salicylic acids have been investigated. From an analysis of the spectra of these compounds along with those of their deuterated analogues, sodium salts and hydrochlorides, it has been found that the *m*-amino salicylic acid has a zwitterionic structure in the solid state while the *p*-amino derivative is normal.

Hydrogen bonding in hydroxyflavones and isoflavones was further investigated by a study of their BF_3 adducts and the solvent effect. In support of earlier results, it was found that the 5-OH derivative is strongly hydrogen bonded to the carboxyl group while the 3-OH groupshowed little hydrogen bonding.

Infrared spectra of metal chelates of *o*-amino benzene sulphonic acids have been analysed. The amino wagging mode and the splitting of the degenerate SO_3^- stretching modes were found to be sensitive to the metal ion and follow the well known Irving-Williams order of stability namely $Mn < Co < Ni < Cu > Zn > Cd$ in these complexes.

The band intensities of aromatic bands at 1600 and 1580 cm^{-1} in *p*-substituted methyl benzoates and 1,2,4-phthalic esters with different electron donor and acceptor groups were measured. The band intensities which were found to depend on the nature of the substituted group are being correlated with proton chemical shifts.

The origin of two bands in the carboxyl region in cholestanol esters (3β, 5α, 6β-triol, 3 methyl ether 6-acetate and 6-benzoate) in solution was investigated by measuring the intensities of the carboxyl and hydroxyl bands at various concentrations. It was found that these two bands arise from intermolecular association. A study of model compounds (cholestane 5α 6β-diol 6-acetate, 3β-methoxy 5α-hydroxy cholestane, 5α hydroxy cholestane, cholestane 5α 4 β-diol 4-acetate and 5α 6β-diol 6-acetate) under similar conditions and some studies in dioxan solution confirmed the above conclusions.

A low temperature infrared cell for the study of spectra of low boiling liquids and a Macleod gauge for noting the pressure in such cells have been fabricated.

5. THERMODYNAMIC STUDIES

5.1 *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 adiabatic compressibility of dilute aqueous solutions of methacrylic acid, polymethacrylic acid and three polysodium methacrylate (obtained by neutralizing the polyacid with sodium hydroxide to different extent) were determined from ultrasonic velocity and density data. The ultrasonic velocity at 25° was measured employing a precision ultrasonic interferometer and the density was measured with Ostwald-type pyconmeters. The nature and the number of the free counter-ions and the shape and concentration of the polymer molecules were both found responsible for the compressibility of the polymer solutions. However, the contribution of the size and shape and concentration of the polymer seemed to be less than that of the nature and number of the counter-ions. The apparent molal volume $\phi\underline{V}_2$ and the apparent molal compressibility $\phi\underline{K}_2$ for the polymer repeat unit showed a sharp decrease with increase of concentration. This might be explained by the fact that in dilute region the polymer, extended by coulombic repulsion between similar charges situated on the side chain, enhanced formation of water clusters around it and the free counter-ions are also solvated. The number of free counter-ions proportionately increased with concentration causing a proportional decrease of $\phi\underline{V}_2$ and $\phi\underline{K}_2$ values until the concentration reached a definite stage above which the so-called condensation of ions occurs and the number of free counter-ions does not increase further at higher concentrations. Work on some other structurally similar polymers such as polymethacrylamide etc. is being carried out.

6. NUCLEAR AND RADIATION CHEMISTRY

6.1 *Effect of radiation on chemical reactions :* (AB-12/67)

Radiolysis of benzene + water : A thorough restudy of this old system showed the true G (phenol) to be 1.5 (and not 2.6 as often reported) which is nearly independent of temperature up to 60°. Ferrous ion at a concentration of 10^{-3}M increased the G value to 8.5 due to a mild chain reaction involving peroxy redicals.

Radiolysis of naphthalene and water : It was proved that this system is identical in behaviour with the aqueous benzene system if the solubility of naphthalene is increased by sealing off the irradiation vessel and raising the temperature. Thus at 130° the G value of naphthol rose to 1.4 from the room temperature value of 0.025. Hence a chain reaction with naphthalene is expected wherever benzene indicated one.

Radiolysis of naphthalene + 1 normal aqueous ammonia : G value of naphthylamines rose from 0.1 to 0.5 in the range 110-175°.

Naphthylamines were estimated by diazotisation and coupling with β-naphthol, and phenol by coupling with diazotised *p*-nitroaniline. The extinction coefficient for phenol and α-naphthylamine was 25,000 and for β-naphthylamine 19,000.

Thermal chain reaction between alcohol and aromatic hydrocarbons : Benzene or naphthalene, with ethyl or methyl alchol at 300^c, yielded phenol or naphthol in a chain reaction involving the participation of oxygen. With naphthalene, 0.2% conversion to a ~3:1 mixture of α- and β-naphthols was obtained in one hour for a 1:1 mixture of naphthalene and alcohol. In the case of benzene the phenol yield was maximum (1.5%) for 94.5 mole % benzene in alcohol. All the reactions were carried out in presence of air.

6.2 *Mössbauer spectroscopy :* (B-3.1 and 3.2/67)

On the basis of the results reported earlier on the Mössbauer spectra of spinel type compounds containing either a ferrous or a ferric ion on only one of the two non-equivalent sites, the cation distribution in the partially inverse spinel $FeAl_2O_4$ could be determined from its Mössbauer spectrum. The degree of inversion (23%) determined from the Mössbauer spectrum was found in good agreement with the value (25%) determined from the X-ray powder pattern. The degree of inversion was further found to be independent of temperature from – 194° to 400°.

Mössbauer effect studies have also been used to identify the charge distribution in mixed oxide systems with spinel structure viz. $ZnMnFeO_4$ and $CoMnFeO_4$ where Fe, Co and Mn can exist in a number of possible valency states, viz. +2, and +3, +2 and +3; and +3 and +4 respectively. The charge distribution in the above mixed oxide systems has been found to be as follows :

(a) $Zn^{2+}\ Mn^{3+}\ Fe^{3+}\ O_4$

(b) $Co^{3+}\ Mn^{2+}\ Fe^{3+}\ O_4$

6.3 *Diffusion in solid state :* (B-2.1/67)

Diffusion coefficients of the rare earth elements Promethimum-147, Terbium-160, Thulium-170 and Lutetium-177 in copper metal were determined in the temperature interval 700-950° by the residual activity method and Gruzin's method of analysis where the diffusivity D is calculated by the expression

$$(\mu I_n = \frac{dI_n}{dx_n} = \text{constant x exp} (-x^2/4^{Dt})$$

where μ is the linear absorption coefficient in cm^{-1}. In the radioactivity at a depth x_n and t is the annealing time in seconds. The values of the diffusion coefficients of ^{147}Pm, ^{160}Tb, ^{170}Tm and ^{177}Lu in copper metal as a function of temperature could be expressed by the following expressions :

$$D\,(^{147}\mathrm{Pm}) = 7.089 \times 10^{-9} \exp\,(-24{,}495/RT)\ \mathrm{cm}^2\ \mathrm{sec}^{-1}$$
$$D\,(^{160}\mathrm{Tb}) = 1.009 \times 10^{-9} \exp\,(-23{,}132/RT)\ \mathrm{cm}^2\ \mathrm{sec}^{-1}$$
$$D\,(^{170}\mathrm{Tm}) = 2.132 \times 10^{-9} \exp\,(-22{,}495/RT)\ \mathrm{cm}^2\ \mathrm{sec}^{-1}$$
$$D\,(^{177}\mathrm{Lu}) = 3.375 \times 10^{-8} \exp\,(-29{,}191/RT)\ \mathrm{cm}^2\ \mathrm{sec}^{-1}$$

The activation energies for the diffusion of Pm, Tb, Tm and Lu in copper are found very much lower than the activation energy for the self-diffusion of copper. It appeared that the diffusion is taking place through the short-circuiting dislocation paths and this may be due to low solid solubility of the rare earth elements in copper.

The sectioning method of diffusion studies has also been standardized. The values of the diffusion coefficient of ^{57}Co in copper determined by the residual activity method and the sectioning method are found in agreement with one another and with those reported in literature by other workers.

7. SYNTHETIC INORGANIC CHEMISTRY

7.1 *Titanium and tin organics :* (AB-14/63)

The scope of this project was outlined in the last year's report. More sigma-bonded Ti-C compounds were synthesized by partial chelation of the quadrivalent titanium atom. In general, the alkyltitanium compounds showed lower stability of the Ti-C bond than the aryl ones, and some of them were probably mixtures, though once prepared they appeared to be quite stable if moisture was rigorously excluded. The study is continued.

On Ti-O-C type compounds, the investigation was extended to alicyclic polyol ligands. Cyclohexane 1:4 diol (LH_2) alone gave three compounds $(LH)_2TiCl_2$, $LTiCl_2$ and LTi_2Cl_6 under different reaction conditions. Other cyclohexane diols are under study.

As a result of enquiry from a firm dealing in metal organics, the synthetic techniques being developed for titanium organics have recently been extended to include organotin compounds. The use of organotin compounds is well established in the polymer industry, and millions of pounds of tin organics are synthesized every year for use in polymerization catalyst systems and as stabilizers. There are also some significant features of more fundamental interest in the structural chemistry of tetravalent titanium and tin, though they belong to different sub-groups of the periodic system, which call for basic research in this well-defined area.

7.2 *Coordination polymers :* (B-6/63)

Titanoxane polymers containing cyclopentadienyl group and a univalent bidentate chelating ligand like 8-quinolinol and acetoacetanilide were synthesized. These insoluble polymeric materials have been characterized by their elemental analysis and IR spectra. TGA showed that they decompose very slowly initially but rapidly after 375°. After 470-80°, there is no further loss in weight, the total weight loss corresponding to theoretical conversion to TiO_2. On the basis of elemental analysis, the polymeric products obtained from 4.6-diacetylresorcinol and titanium tetra-alkoxides, $Ti(OR)_4$ [$R = C_2H_5$, C_3H_7, C_4H_9], were characterized. Cu(II), Ni(II) and Co(II) also gave polymeric materials having 4,6-diacetylresorcinol backbone. TGA of these polymeric materials showed that the copper polymer loses 15% of its weight at 230°, nickel loses 23% at 250° and cobalt loses 25% at 300°. The work on coordination polymers of titanium, tin and zirconium with *bis*-[8-hydroxy-5-quinolyl]-methane has been reported.

7.3 *Spectral studies of coordination compounds :*

Work on visible and ultraviolet spectra of copper chelates of 1,1,1-trifluoroacetylacetone, 3-nitroacetylacetone, ethylacetoacetate, acetoacetdiethylamide, acetoacetanilide and acetoacet·orthochloroanilide in a large number of solvents has been completed. Proton magnetic spectral studies on acetoacet·diethylamide and its beryllium chelate have been carried out. Enol content of acetoacet·diethylamide has been determined in carbon tetrachloride (calculated graphically and by integration) and has been found to be 56.10%. Low enol contents of the liquid acetoacet·diethylamide as such (40.00%) and of its solution in deuteroacetone (24.5%) suggested the enol to be less polar and hence hydrogen bonded.

7.4 *Coordination compounds :*

Their reactivity and isomerism : Work on organomercury compounds isolated during the course of our studies of mercuration in some β-dicarbonyl compounds has been reported.

Nickel acetylacetonate is known to react with nitrite ion in the presence of ammonium acetate to give a red diamagnetic square planar crystalline compound. On the basis of mass spectral studies of this compound and of nickel dimethylglyoxime, a new structure has been proposed.

Nitration of beryllium acetoacetanilide has been done and the structure of the nitro compound thus isolated has been confirmed from its NMR spectrum. The nitrochelate exhibited signals at $\tau = 7.25$ and 2.49 corresponding to methyl and phenyl protons respectively but none in the vinyl region.

Chromium(III) chelates of orthochloroacetoacetanilide, 2,5-dimethoxy-4-chloroacetoacetanilide and acetoacet·diethylamide have been synthesized for the first time. Attempts to separate the geometrical isomers of these chromium chelates by utilizing solubility differences and chromatographic technique were not successful showing the instability of the *cis*-isomer.

Considering the growing interest in recent years in cyclopentadienyl metal compounds with gradual development in their industrial applications, work on such compounds has been initiated. *Bis*-(cyclopentadienyl) titanium dichloride was prepared and during attempts to substitute the chlorine atoms with ligands containing N,O and S atoms, compounds e.g. cyclopentadienyl, *bis*-(8-quinolinolato) titanium(IV) chloride, (π-C_5H_5)Ti (OX $)_2$Cl, acetoacetanilidato *bis*-(cylopentadienyl) titanium (IV) chloride, (π-C_5H_5 $)_2$ *Ti* (acacN) Cl and 1,3-diphenyl-1,3- propanedionato, *bis* (cyclopentadienyl) titanium(IV) chloride, (π-C_5H_5 $)_2$Ti (dbzm)Cl were synthesized for the first time. Infrared spectra of these compounds showed the chelation of the ligand to the metal.

7.5 *Infrared spectra of metal chelates :*

Work on the infrared spectral studies of salicylaldoxime and some of its metal chelates has been published. The infrared spectra of acetoacetanilide chelates of Cu (II), Be (II), Cr (III), Al(III), Fe(III) and Ti(IV) in the region 700 cm^{-1} – 400 cm^{-1} have been examined using CsBr prism. The metal–oxygen stretching vibrational modes have been located in the 400-500 cm^{-1} region in these complexes. Infrared spectra of Cu(II), Mn(II), Ni(II), Co(II) and Cr(III) chelates of *o*-hydroxy-benzoyl *o*-hydroxybenzal hydrazide have been recorded.

7.6 *Polarographic studies of copper chelates :*

The polarographic behaviour of a few copper chelates, for instance, copper acetoacetanilide, copper acetoacet·diethylamide, copper acetoacet·orthochloroanilide, copper nitroacetylacetonate, copper trifluoroacetylacetonate and copper ethylacetoacetate was studied in 50% pyridine-water, 75% dioxane-water and 50% methanol-water solutions. The $E_{\frac{1}{2}}$ values were used to compare relative stabilities of the compounds. It was found that the nature of the solvent influences the reduction of the chelates. Attempts are being made to calculate the accurate stability constant values by the potentiometric method.

7.7 *Fluorine chemicals :* (AB-15/63)

Although benzotrifluoride is non-reactive to electrophilic aromatic substitution, the compound has been mercurated using a solution of mercuric perchlorate. The mercurated product was reacted with bromine (to give mainly *m*-bromo-benzotrifluoride) and also with acetic anhydride which yielded as yet unidentified products.

Electrochemical fluorination of acetic anhydride was carried out with partial success. The difficulty was mainly due to defects in the cooling system (resulting in considerable losses of anhydrous hydrogen fluoride) and the low amperage capacity of the cell. A new apparatus, using a pack of square electrodes separated by teflon spacers and having one single surface and one double surface condenser, has been fabricated.

The fabrication and installation of a cobaltic fluoride fluorination reactor has been completed.

An apparatus has been fabricated for making dry hydrogen fluoride by the thermal decomposition of potassium bifluoride. This apparatus is put to regular use for inorganic hydrofluorinations inside a nickel reactor.

Attempts to oxidize benzotrifluoride with air using a vanadium pentoxide/ molybdic acid/alumina catalyst, as done in the commercial oxidation of benzene to maleic anhydride, failed, presumably on account of the presence of the electron-withdrawing trifluoromethyl group.

8. PHYSICO ANALYTICAL CHEMISTRY

8.1 *New reactions of analytical importance :* (AB-16/66)

In addition to and in support of the analytical service provided by the group the following investigations have been carried out during the year under review.

8.1.1 *Selective electrodeposition of Co from a solution of Co and Ni :* A new method has been developed for the selective deposition of Co from a solution containing cobalt and nickel. The method consists in depolarizing the cathode by introducing nitrate ions into the bath and complexing the Co(II) with malonic acid. Incorporation of perchlorate ions in the medium completely prevented the reduction of nickel ions. Studies on the mechanism of the reaction are in progress.

8.1.2 *Extraction of cobalt by liquid ion exchange :* Cobalt in solution, when treated with malonic acid and sodium nitrite, forms an anionic complex mentioned in our previous report. This reaction has been utilized for the separation of cobalt from nickel by liquid ion exchange using tri-*n*-octylamine.

8.1.3 *Polarographic behaviour of coordinated ligands* : An interesting observation has been made in the polarographic reduction of the uncoordinated oxime group of the malonic acid oxime complex of cobalt $[\, HON{=}C(COO)_2\, Co^{II}\, NO_2\, (H_2O)_3\,]\,Na$. The bound ligand is reduced at a more positive potential than the free ligand. Reduction behaviour of similar coordinated ligands are in progress.

8.1.4 *Molybdenum catalysed hydrogen waves at dropping mercury electrode* : From millimolar hydrochloric acid solutions containing ammonium molybdate (5×10^{-5} M Mo) a well developed catalytic hydrogen wave appeared before the normal hydrogen discharge. While the $E_{\frac{1}{2}}$ value of this catalytic step remained at -1.05V vs SCE, the height of the step increased with molybdate concentration. Surface active agents, complexing agents and certain buffers suppressed the catalytic wave. In the range of hydrochloric acid concentration in which the catalytic wave persisted, i.e. between pH 2 and 5, the height and shape of the wave changed with pH. The kinetic nature of the wave is confirmed by the comparatively high temperature coefficient of the limiting current (4% per degree) as well as its lack of dependence on the mercury pressure.

9. NATURAL ORGANIC PRODUCTS

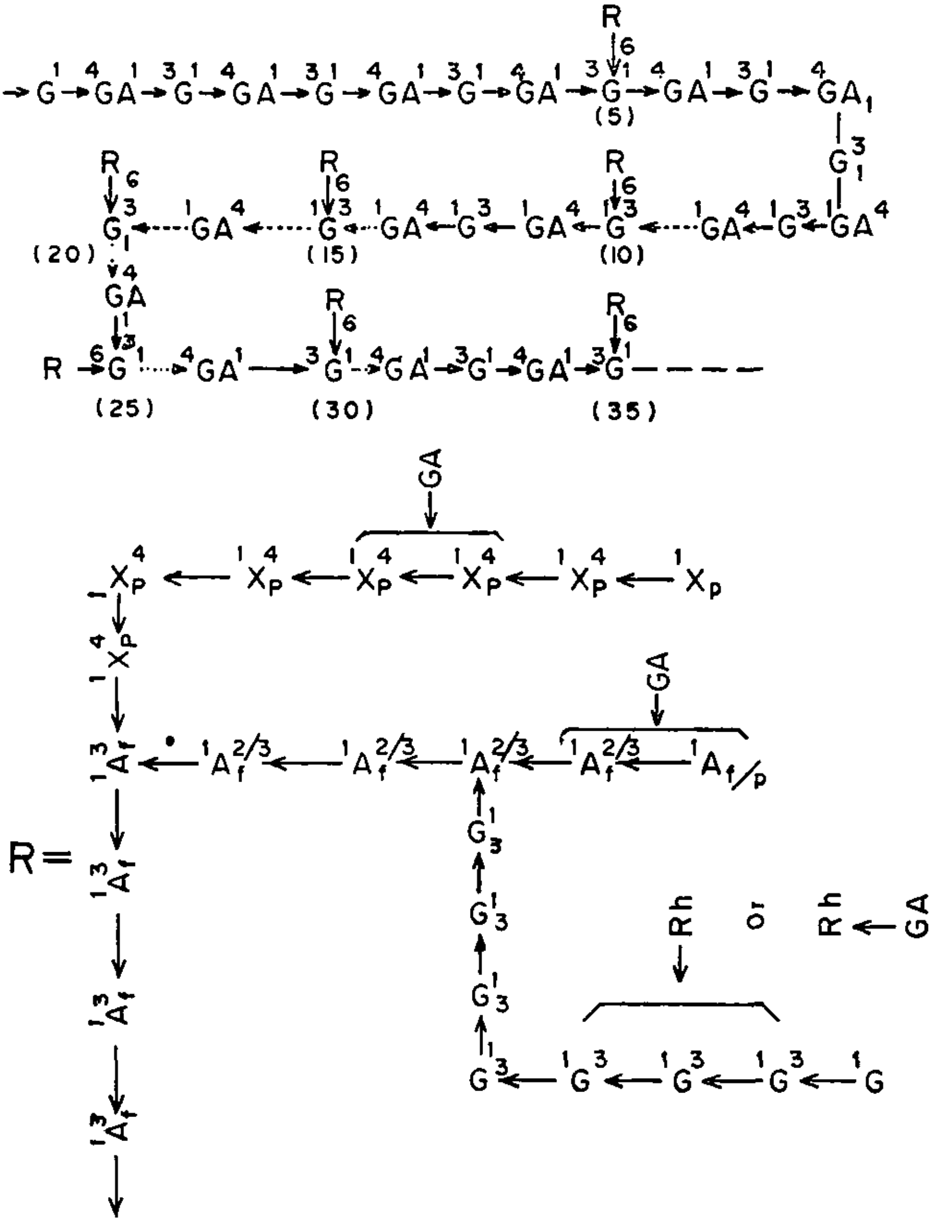
9.1 *Terminalia tomentosa gum* (Mar.: Ain) (AB-23/65)

This gum is available in large quantities in the country and is not much in use. Investigation on the structure of this gum was undertaken with a view to find whether its structure could be suitably modified to make it acceptable to industry.

The gum has been found to be composed of D-galactose, L-arabinose, D-xylose and D-galacturonic acid and traces of L-rhamnose. From a study of its partial degradation, periodate oxidation, and methylation and products of methanolysis, a tentative structure has been assigned to the gum (Fig. on p. 62.)

A part of the work involving vapour phase chromatographic studies and identification of methanolysis fragments has been carried out in collaboration with Trent University, Canada and University of Edinburgh, Scotland.

STRUCTURE OF
TERMINALIA TOMENTOSA GUM



G = D GALACTOSE
A = L - ARABINOSE
Rh = L - RHAMNOSE
GA = D - GLUCURONIC ACID
X = D - XYLOSE
R = SIDE CHAIN

9.2 *Celastrus paniculatus :* (AB-18/67)

The total polyester present in *Celastrus paniculatus* has been found to possess valuable pharmacological properties. A large sample of this material has been prepared and supplied to Repoproductive Physiology Unit, G. S. Medical College, Bombay, for further evaluation. Two pure compounds have been isolated from the total polyester and their structure elucidation is in progress.

RP 9.3 *Utilization of β-himachalene :* (AB-17/67)

β-Himachalene, the chief component of the readily available Indian deodar oil (*Cedrus deodara* Loud.), is potentially a valuable substrate for preparing compounds of possible commercial utility. With this aim in view pyrolysis of β-himachalene has been carried out and cuparene has, thus been prepared in a single step. The identification of other products is in progress.

9.4 *Utilization of by-products of opium alkaloid industry :* (AB-21/67)

9.4.1 *Preparation of steroidal hormone analogues from cyclolaudenol:* Cyclolaudenol and cycloartenol are present in considerable quantities in the opium marc and a method has been standardized for their isolation. Transformation of both cyclolaudenol and cycloartenol into steroidal hormone analogues is in progress.

9.4.2 *Conversion of thebaine into codeine :* Thebaine, a by-product of morphinecodeine manufacture from opium, has practically no medicinal use. Work is in progress for its conversion into codeine.

9.5 *Oleoresins and resinoids :* (B-7.1/67)

Only preliminary work on two resins (*Pinus longifolia* and *Vateria indica*), both of commercial importance, has been carried out. It has been found that the acids present in the oleoresin of *Pinus longifolia* are not of abietic acid type and belong mostly to the pimaric group.

The resin of *Vateria indica* has been found to be an exceedingly complex mixture of several triterpene hydrocarbons, ketones, alcohols and acids, along with small amounts of sesquiterpenes.

9.6 *Wood extractives :* (B-7.2/67)

Preliminary work on *Osyris arborea* showed that the wood contained a fragrant sesquiterpene alcohol having a useful sandalwood odour. Since in the Santalaceaae family, it is only usually the heartwood contains the essential oil, arrangements are being made to get some stumps of this wood for extraction of this alcohol on a larger scale. A number of fatty acids besides mannitol, have been identified in the wood.

9.7 *Flavonoids :* (B-8.9/58)

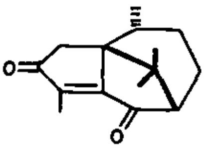
The structures assinged by Sondheimer and by Dreyer and Bertelli to zapotin and zapotinin have been confirmed by synthesis.

9.8 *Cyperus scariosus* (Mar. : Nagarmutha) *:* (B-7.5/64)

A systematic chemical examination of the oil from the roots of this plant has been undertaken.

The oil has been shown to be a mixture of at least 15 sesquiterpenic components. A striking feature of this oil is the occurrence of a large number of tricyclic sesquiterpenes. New crystalline sesquiterpenes such as isopatchoulenone, cypernol and patchulenol isolated and characterized from this oil have been reported earlier. A new crystalline sesquiterpene dione scariodione has been isolated and characterized.

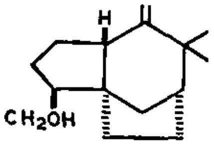
Several known sesquiterpene hydrocarbons such as cyperene, α and γ-patchoulenes and a known ketone patchoulenone have also been isolated and characterized.



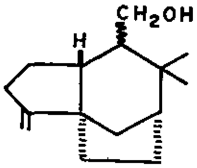
Scariodione

9.9 *Vetiver oil* (Hin. : Khus) *:* (B-7.4/60)

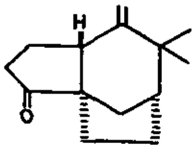
Several varieties of Indian vetiver oil have been examined for the isolation and characterization of its constituents. The dextrorotatory South Indian vetiver oil has yielded several new perfumery alcohols and ketones having new carbocyclic system. The structures of khusimol, isokhusimol and khusimone have been determined.



Khusimol



Isokhusimol



Khusimone

From the high boiling fraction of the oil, a viscous hydrocarbon, n-eicosane has been isolated and characterized. The high boiling fraction also yielded a tetracyclic sesquiterpenic primary alcohol.

9.10 *Acidic constituents of costus root oil :* (B-7.7/66)

The scheme for converting costic acid into ilicic acid did not lead to any crystalline material and hence the work was not carried out further.

9.11 *Guaicum wood oil :* (B-7.8/67)

Elaborate column chromatography of the guaicum wood oil furnished a tertiary alcohol only in small quantity which is probably the exo-cyclic double bond isomer of bulnesol. The work is now concluded.

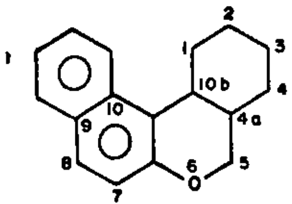
10. SYNTHETIC ORGANIC CHEMISTRY

10.1 *Studies in hydride transfer :* (B-8.7/65)

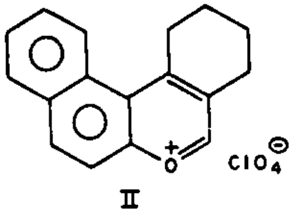
Thiachromans : The work on the hydride transfer reactions yielding thianaphtholenium perchlorates and thiachromans was extended to compounds having a cyclopentene ring fused at the 3,4-junction of the thiachromans. The characterization of the products from the cyclodehydration of phenylmercaptomethylcyclopentanones is in progress.

The synthesis of substituted chromans starting from phenol and *m*-methoxyphenol was reported earlier in connection with the work on the stereochemistry of hydride transfer at the ring junction. This work was extended to compounds starting from β-naphthol. Thus 2-(β-naphthoxymethylene) cyclohexanone after catalytic hydrogenation and cyclization gave a mixture of 9,10-benzo-6-oxa-1,2,3,4, 4a,5,6,10b-octahydrophenanthrene (I) and 9,10-benzo-1,2,3,4-tetrahydro-6-oxa-phenanthrinilium perchlorate (II). The percentage composition of *cis/trans* isomers in (I) is being examined.

The stereo-electronic factors which control the directive effects of nucleophilic attack on the naphthopyridium nucleus were investigated. Thus the sodium borohydride reduction of perchlorates (III, IV, V and VI) gave mixtures of 1H and 3H pyrans; the ratios of 1H:3H were determined by NMR and were found to be 44:56, 5:95, 82:18 and 20:80 for compounds III, IV, V and VI respectively. The steric and electronic factors which contribute to the above product pattern will be discussed in a forthcoming publication.



I



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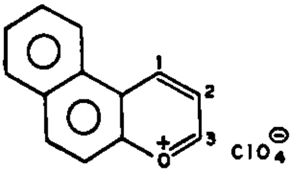


III

IV 1-methyl
V 3-methyl
VI 1,3-dimethyl

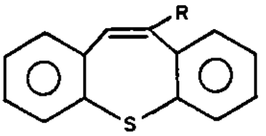
10.2 *Vat dyes :* (B-8.8/62)

It is argued that cyclizations of the Scholl type whereby two aryl nuclei are linked by a dehydrogenative process in presence of strong Lewis acids like $AlCl_3$, leading to the formation of a cyclic structure may proceed through a hydride transfer mechanism. This theory is being put to test and attempts are in progress to collect experimental evidence for or against such a hydride transfer process. Two typical examples chosen for study are. (a) the cyclization of anthrimide to a carbazole derivative as in the case of Vat Olive R and (b) the formation of Vat Golden Yellow GK from the *trans* ketone.

10.3 *Biologically active compounds :* (B-8.31/68)

The studies on the synthesis of bicyclic thiaxanthylium perchlorates were continued. The reaction of diazomethane on 9-phenylthiaxanthylium perchlorate led to a 60% yield of (I) whose structure was confirmed on the basis of spectral evidence (NMR, IR and MS). The reaction presumably involves the nucleophylic attack by the carbene generated by the decomposition of diazomethane. Several 9-substituted derivatives have been so treated to yield compounds of the type (I).

The biological testing of the several new compounds prepared during the past two years has been undertaken.



R = phenyl, methyl etc.

(I)

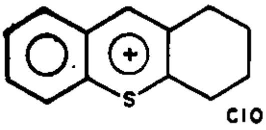
10.4 *Anti-fertility drugs :* (AB-25/66)

The attempts to build the 11-thiasteroidal skeleton were continued. The synthesis of the thiophene analogue of stilbestrol was undertaken. The key intermediate for this synthesis, 2-methoxy-5-propionylthiophene was prepared and characterized.

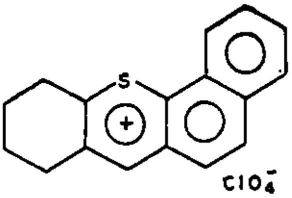
10.5 *Carcinostatic compounds :* (B-8.32/68)

The studies on the preparation of sulfur analogues of 3,4-benzophenanthrene in which the sulfur atom occupies 1 or 2 positions in the phenanthrene nucleus were continued.

Phenyl-, α-naphthyl-mercaptomethylenecyclohexanones and phenylmercaptomethylene-α-tetralone were synthesized. On treatment with 70 % perchloric acid they yielded the linear heterocyclics (I), (II) and (III) respectively, instead of the corresponding angular thiaphenanthrenium salts. A mechanism of formation of these unexpected products was proposed. The dehydrogenation of the above perchlorates to the heteroaromatic systems is in progress.



I



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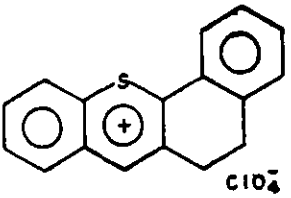
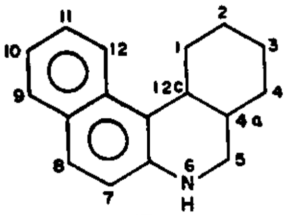


III

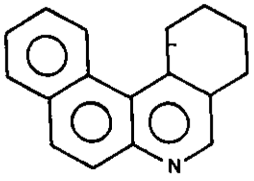
The stereochemistry of the various mercaptomethylenecyclohexanones was studied and they were found to have a *cis*-configuration (vinylic proton is *trans* to the carbonyl group). The products obtained by the interaction of thiophenol with hydroxy or ethoxymethylenecyclohexanones under acid or base catalysis were identical.

The synthesis of polycyclic nitrogen heterocycles was continued. The cyclodehydration of β-naphthylaminomethylcyclohexanone in presence of polyphosphoric acid gave a mixture of 1,2,3,4,4a,5,6,12c-octahydro-benzo (a) phenanthridine (IV) and 1,2,3,4-tetrahydrobenzo (a) phenanthridine (V). Whentriphenylchloromethane was employed in the above reaction as an external hydride abstractor, a stable molecular complex of (V) and triphenyl carbinol was obtained from which (V) could be isolated. α-Naphthylaminomethylcyclohexanone underwent identical reactions as in the case of β-naphthyl analogues yielding mixtures of octahydro- and tetrahydro-benzo (c) phenanthridine derivatives. The tetrahydroderivatives were dehydrogenated with selenium to benzo (a) phenanthridine and benzo (c) -phenanthridine.

Attempts to cyclise 2-anilinomethyl-1-tetralone or the corresponding alcohol have so far failed and other possible routes are being examined.



IV



V

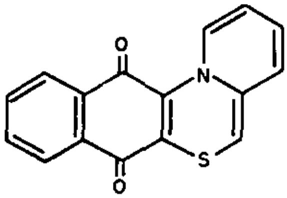
10.6 *Potent analgesics :* (B-8.33/68)

The synthesis of potential analgesics of the dithienylbutenylamine type was continued. The synthesis of 4-phenyl- and 4-thienyl-7-methoxyquinolines were reported earlier. As an extension of this programme, 3,4-dimethyl- and 3-methyl-4-phenyl-7-methoxyquinolines were synthesized and characterized. The corresponding tetrahydro derivatives of the above quinolines have been prepared.

The sodium borohydride reduction of the quinolinium methiodides have resulted in the exclusive formation of 1-N-methyl-1,2-dihydroquinolines which were found to be unstable. In order to isolate the stable dihydro derivatives, the effect of various substituents in the heteroaromatic ring leading to a stable dihydro compound was investigated. Thus, phenyl, thienyl, methyl and cyclohexyl substituted compounds were synthesized. The biological activity of the various compounds synthesized is under evaluation.

10.7 *New heterocyclic vat dyes :* (B-8.21/68)

The synthesis of the hitherto unreported ring system, *viz.* 3,4-phthaloyl-2-thiaquinolizine (I) was achieved starting from 2,3-dichloro-1,4-naphthoquinone and 2-mercaptomethylpyridine. Attempts are in progress to prepare the 1-carbethoxy derivative of (I) which would be of interest for the synthesis of disperse dyes.



(I)

10.8 *Studies on the reduction of quinones :* (B-8.20/67)

It was observed earlier in this Laboratory that the sodium hydrosulphite reduction of dianthrimide under certain conditions causes a breakdown of the anthrimide linkage. It is currently believed that the alkaline hydrosulphite reductions proceed through a free-radical mechanism and an examination of this type of reduction has been undertaken. Several intersting intermediates have been isolated from dianthrimide itself and their structures are being examined. It is also proposed to extend this study to several substituted anthrimides.

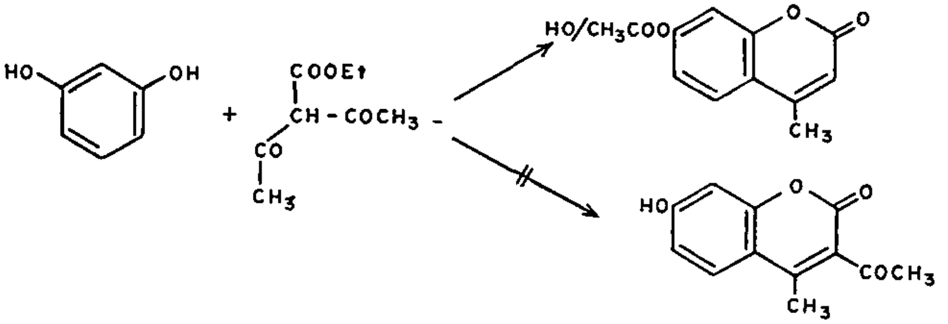
10.9 *Naturally occurring anthraquinone pigments :* (B-8.10/64)

Two new pigments, designated as cassiamin B and C, have been isolated from *Cassia siamea.* Like cassiamin A, cassiamin B and C are derivatives of 2,2′-bianthraquinonyl, two molecules of emodin and two molecules of chrysophenol respectively being linked together.

Kermesic acid : Kermesic acid, the colouring matter of an insect, very similar to the lac insect; is a dye of very great antiquity. Dimroth's structure has to be modified and the correct structure is 1,2,4,7-tetrahydroxy-5-methyl anthraquinone-6-carboxylic acid. Xanthokermesic acid, identical with laccaic acid D, built from one acetate and seven malonate units, plays a central role in the biosynthesis of kermesic acid, carminic acid, the laccaic acids, the erythrolaccins and ceroalbolinic acid.

10.10 *4-Acetomethylcoumarins* : (B-8.3/66)

In the course of studies initiated for the confirmation of the disputed 4-acetomethylcoumarin structure assigned to the Kostanecki-Robinson acetylation products of orcacetophenone and its derivatives, various attempts were made to obtain the elusive 3-acetylcoumarins. In one of these attempts resorcinol was condensed with ethyl acetylacetoacetate in the presence of a mixture of phosphorous oxychloride and anhydrous zinc chloride. One of these reactions led unexpectedly to the formation of 4-methyl-7-acetoxycoumarin; others giving the deacetylated product (I). The possible mechanism of this reaction is under investigation.



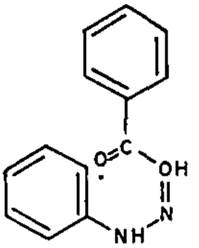
10.11 *Synthetic studies in 4-arylcinnolines* : (B-8.4/64)

Cyclodehydration of the *cis*-isomer of phenylglyoxal-2-phenylhydrazone (I) with molten aluminium chloride-sodium chloride was found to give a mixture of almost equal quantities of two isomeric products which were easily separable by chromatography. The two products were found to be identical with 4-phenylcinnoline (II) and 2-phenylquinoxaline (III) respectively by a direct comparison with the authentic products synthesized by standard methods. The *trans*-isomer was also found to undergo the same transformations.

The product obtained earlier in this Laboratory by a similar cyclodehydration of *o*-hydroxyphenylglyoxal-2-phenyl-hydrazone has now been assigned the structure of 4- (*o*-hydroxyphenyl)-cinnoline. Re-examination of the earlier work revealed that although traces of cinnolines are formed in these reactions (TLC), the main products were, in fact, the isomeric 2-(*o*-hydroxyphenyl)-quinoxalines (mass spectra and TLC mobility). This has been confirmed by a direct comparison of the product obtained by cyclization of *o*-hydroxyphenylglyoxal-2-phenylhydrazone with 2-(*o*-hydroxyphenyl)-quinoxaline recently synthesized by a different known method.

Isomeric cinnolines and quinoxalines, which are difficult to distinguish otherwise, were found to have different mass spectral fragmentation modes by which they can be distinguished and identified.

This unusual transformation of phenylglyoxal-2-phenylhydrazones to 2-phenylquinoxalines can be explained by a mechanism involving Dewar structure as advanced earlier in this Laboratory for other similar transformations.



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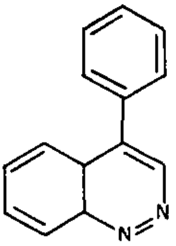

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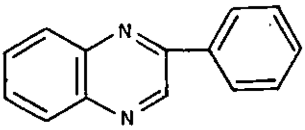


III

10.12 *Synthetic dyes :* (B-8.8/62)

10.12.1 *Azoic dyes :* Mass spectral fragmentation of a number of azo compounds has been studied with the object of elucidating the structures of azo and azoic dyes. The structures of three new " Naphthols " have been determined.

In collaboration with the CIBA Research Centre, it has been found that the acid from which Naphthol AS-LB is prepared is 2-hydroxycarbaxole-1 and not 3-carboxylic acid.

10.12.2 *Reactive dyes :* By chromatography of the products of reaction of a reactive dye of the vinylsulphone type with α-methylglucoside four fractions were separated (60, 20, 7 and 10 per cent respectively). Using NMR spectral data, unequivocal evidence was obtained for their being the products of reaction with the C (6), C (2), C (4) and C (3) hydroxyl groups. Similarly it is shown that in dyed viscose the primary hydroxyl and C (2) hydroxyl groups of cellulose are the main sites of attack, the relative amount of the products being 60-70 and 40-30 per cent.

NMR spectral evidence has shown that cellulose forms ether linkages with reactive dyes of the vinylsulphone type and ester-type linkages with reactive dyes of the monochloro- and dichlorotriazine type.

To assign the signals of different protons in D-glucose derivatives, several derivatives of methyl α-D-glucopyranoside substituted different positions were synthesized and NMR spectra of these compounds were studied. Attempts were made to hydrolyse viscose and cellulose dyed with procion dye in order to isolate compounds containing D-glucose and dye units

10.12.3 *Vat dyes :* The structures of some polycyclic quinones such as vat dyes have been solved, mainly by using NMR and mass spectra. The use of NMR spectroscopy is limited by their poor solubility; but it was found that many violanthrone derivatives for instance, as their reductive mathylation products possess adequate solubility in tetramethylurea. The reductive methylation products, from which the parent quinones are easily regenerated, are also useful for chromatographic analysis, using solvents such as benzene. By this technique, it has been possible to show that bromination of 16,17-dimethoxyviolanthrone gives the the 3,12-dibromo derivative.

From the mass spectral fragmentation of the reductive methylation product of Indanthrone Navy Blue G (CI 71200), it has been confirmed that the dye has a monomeric structure.

NMR and mas spectral data have shown that the structure assigned earlier to Cibanone Orange R is to be revised. It is probably 2,4, *bis*-β-anthraquinonyl-1,3-dithiocyclobutane, but further evidence is being sought.

10.12.4 *Arylation of anthraquinone derivatives :* In connection with the structures of the laccaic acids and the possibility of synthesizing useful acid, disperse and reactive dyes, the arylation of anthraquinone derivatives is being studied.

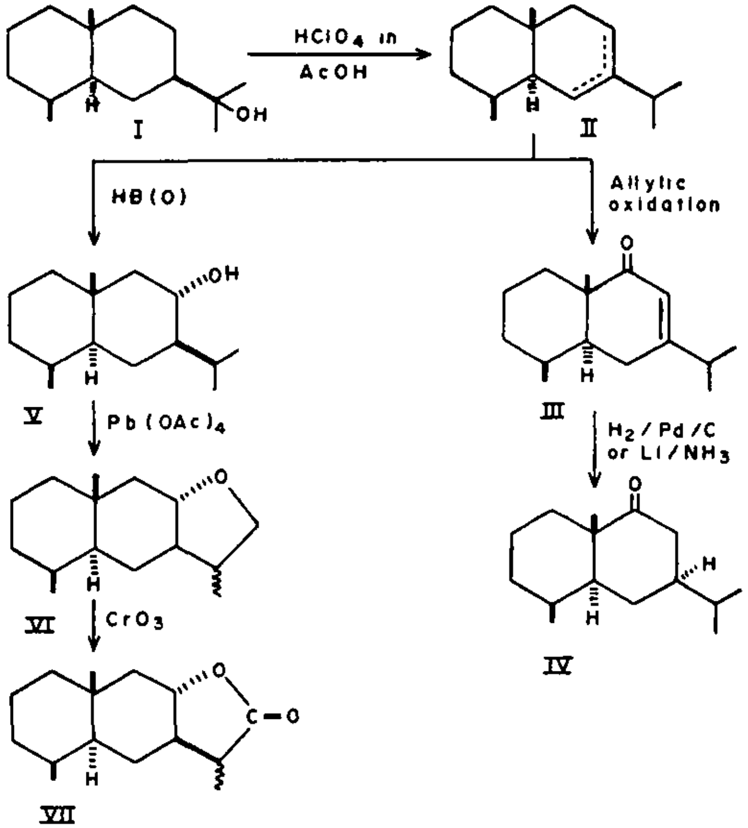
10.12.5 *Marschalk reaction :* The mechanism of the Marschalk reaction and its technical possibilities are being studied. The action of formaldehyde and sodium dithionite on purpurin-2-methyl ether yielded 2,3-dimethylquinizarin. The structures suggested for the tautomeric intermediates obtained from purpurin by reduction under acid and alkaline conditions have been confirmed by NMR spectral data.

10.13 *Base-catalysed reaction of lithioethylenediamine* : (B-8.18/61)

Stigmasterol on treatment with N-lithioethylenediamine yielded a mixture of isomeric sterols resulting from the migration of the *trans* disubstituted double bond, the 5,6-double bond, however, remains unaffected. Oppenauer oxidation of the isomerized sterols gave a mixture of α-β-unsaturated ketones. By selective ozonolysis, a mixture of androstenedione and projesterone has been obtained. Androstenediones has been separated in pure form while projesterone was only identified by comparative TLC analysis.

10.14 *Transformation products of eudesmol* : (B-8.27/68)

In continuation of the work on the transformation products of eudesmol, eudesmol was converted to the lactone of α-hydroxy-eudesman-13-oic acid (VII) and 9-keto eudesman (IV). The starting material for both the compounds is the hydrocarbon (II) obtained by the action of perchloric acid in acetic acid and on dihydroeudesmol (I).



The above work was undertaken with a view to relate naturally occurring compounds with eudesmol whose stereochemistry is well established. Thus it was found 9-keto eudesman is not identical with dihydrocannarone - a hydrogenation product of canarone - a natural product isolated in this Laboratory. Similarly the lactone (VII) is obtained from natural products like atractylon, santonin and artimysin.

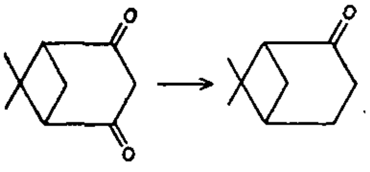
10.15 *Transformation products of carvone and limonene :* (B-8.13/66)

In continuation of our work on the above, selective hydroboration of limonene gave *p*-menthane-6-ene-9-ol disiamyl by disiamyl borane, the rotation of which suggested that it is mainly one isomer. In order to confirm stereochemistry of the new asymmetric centre, attempts are being made to convert it to hexahydrozingeberene through its 9-bromide or 9-*tosyl* derivative.

Carbone when subjected to hydroboration with diborane gave a keto alcohol *p*-menthone-2-one-9-ol. The stereochemistry of this has been proved by converting it to (−) tetrahydrocarvone. This has been extended to study the other derivatives of carvone. Thus carveol with diborane gas gives mainly *p*-menthane-6-ene-2-9-ol. Dihydrocarvone gives a mixture of epimeric *p*-menthane-8-(9)-ene-2-ols in the ratio of 10:1. Disiamyl borane on carveol acetate gives *p*-menthane-6-ene-2-acetate-9-ol. Unlike carvone, carvotane acetone gives mainly in *p*-menthane 6-ene-2-ol. The above reactions indicate that in the hydroboration reaction, the methylenic double bond (8,9) plays a decisive part as observed in case of carvone, carvotane acetone and dihydrocarvone. This is further confirmed by hydroboration of limonene by diborane gas. The reaction will now be extended to bicyclic compounds.

10.16 *Synthesis of bergamotene :* (B-8.17/64)

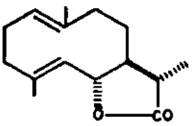
Attempted conversion of the diketone (I) to nopinone (II) did not succeed. Two methods have been tried; (a) LHA reduction followed by oxidation and (b) preparation of enol ether, followed by reduction and hydrogenation.



I II

10.17 *Transformation of costunolide* : (B-8.15/66)

Partial hydrogenation of dihydrocostunolide (I) gave two tetrahydrocostunolides of which one predominates. The major component (II) forms a solid epoxide (III). The compound (II) has also been obtained in pure condition. The minor component appears to be (IV).



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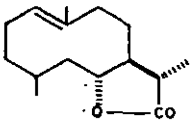

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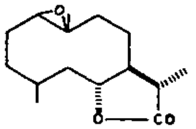
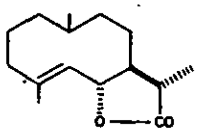


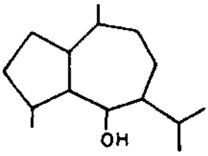
III



IV

10.18 *Transformation of dehydrocostus lactone* : (B-8.19/65)

Dehydration of the monol (I) obtained from dehydrocostus lactone, followed by ozonolysis of the hydrocarbon mixture (II) resulted in formation of mixture of two keto acids (III) and (IV). Attempts to separate the two by preferential semicarbazone formation were not entirely successful.



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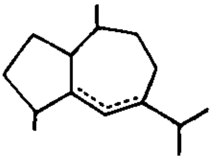

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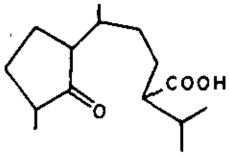

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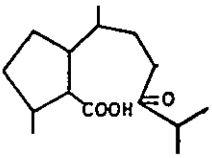
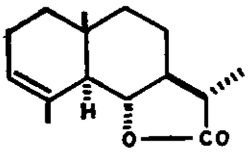


IV

10.19 *Conversion of costunolide into tetrahydrosantonins* : (B-8.14/66)

Direct hydroboration of α-cyclodihydrocostunolide (I) furnishes 3(α) hydroxy santanolide C (II). Oxidation of the latter furnishes β-tetrahydrosantonin (III), which gives α-tetrahydrosantonin (IV), on treatment with acid. Dehydration of (II) furnishes mostly (V). The work is now concluded.



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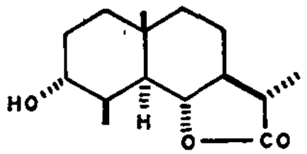

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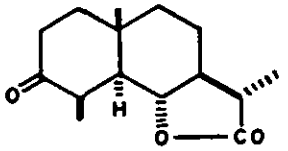

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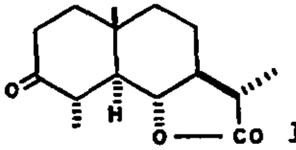

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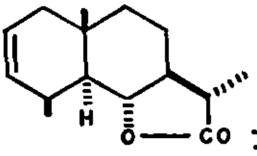


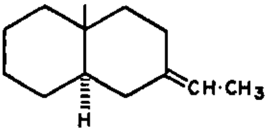
V

10.20 *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 and a few of them such as (–) ∝-santonin are of medicinal importance. Total synthesis of β-elemene, elemol and saussurea lactone have been carried out.

Trans-10-methyl-2-decalone has been transformed to the hydrocarbon (I) and aldehyde (II) employing the appropriate Wittig reagents. The hydrocarbon (I) as well as the aldehyde (II) have been transformed to 4-demethyldihydroeudesmol (III) *via* intermediates which should prove useful in the construction of a variety of C-7 side chains encountered in naturally occurring eudesmanic compounds.

The stereochemistry of methyldihydrocarvone prepared by the addition of lithiumdimethyl copper to carvone has been established.



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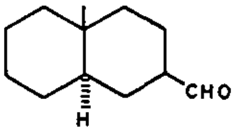

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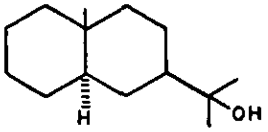


III

11. PHYSICAL ORGANIC CHEMISTRY

11.1 *Mass spectrometry* : (B-5.7 & 5.8/65)

Applications of mass spectrometry : Mass spectral fragmentations of ubstituted anthraquinones, violanthrone derivative and morellin derivatives, some sesquiterpene lactones and oxygen heterocyclic compounds have been studied to explore the possibility of using mass spectrometry as physical probe in elucidating the structure of unknown compounds of these types. Some of the observations were published. Further work is in progress.

Mass spectra of organometallic compounds : The structure of a reaction product of nickel acetyl acetylacetonate has been established only from the mass spectrum of the compound and by comparison with mass spectrum of nickel dimethyl glyoxime. Mass spectral fragmentation of tetra azodisilylcyclohexanes and disilylhydrazines have been examined and new rearrangements reported. The results were published. Other silicon compounds are now being examined.

Skeletal rearrangements : In continuation of our earlier work on skeletal rearrangements, under electron impact, pinacol-pinacolone rearrangement by deuterium labelling and accurate mass measurements have been studied. Also skeletal rearrangements in phenylhydrazones, semicarbazones and thiosemicarbazones have now been supported by deuterium labelling and exact mass measurement techniques.

Stereochemical and tautomerism studies : Mass spectra of azo phenols and quinone hydrazones were examined to study azophenol and quinone hydrazone tautomerism. Mass spectral fragmentation revealed 1,5 hydrogen shifts and rearrangements.

Mass spectral fragmentation of thiosteroids of known stereochemistry were examined to establish difference in fragmentation modes. The work on syn- and anti-bicyclo (2.2.1) heptane derivatives was carried out. A comparison of the spectra of these compounds has shown that mass spectrometry is amenable to structural studies of syn- and anti-isomers. Further work is in progress.

High resolution mass spectrometry : Elemental compositions of some compounds were determined from high resolution mass spectrometry. Different fragmentation modes lending to two different fragments with some nominal mass were resolved by high resolution and their elemental compositions established by accurate mass measurements.

Work on determination of amino-acid sequence in peptides has been initiated. Computer techniques will be used for analysis of high resolution data.

11.2 *Applications of NMR sprctroscopy :* (B-5.2/62)

Studies on conjugated systems : The importance of conjugation and hyperconjugation in certain types of unsaturated molecules has become a matter of considerable doubt. It has been claimed that properties that have been previously attributed to conjugation and hyperconjugation could be explained entirely on the basis of hybridization. Since this question is of fundamental importance to the chemistry of unsaturated compounds, it has been taken up for detailed investigation. The problem was first tackled with the help of nuclear magnetic resonance spectra. The conclusions from this study were later tested with the help of IR spectra.

Long range spin-spin coupling and π-electron distribution : Earlier work from this laboratory has shown that measurements of long range spin-spin coupling may be employed for sensing π-electron distributions in aromatic compounds. Evidence for the unexpected type of bond length changes, that accompany the substitution of nitro- and carbomethoxy groups in the benzene ring, has been obtained using this technique. These changes have been earlier interpreted to mean that there is no conjugation in these systems. However, it has been possible to show that these may more properly be attributed to conjugative interaction between the phenyl and the substituent groups. The same sensing technique has now been extended to the study of donor-acceptor interaction across the benzene ring and the results are under evaluation.

Proton chemical shifts in benzene derivatives and the question of hyperconjugation : Proton chemical shifts of *p*-substituted benzene do not normally show any significant evidence for interaction between the substituent groups even when they are donor-acceptor pairs i. e. a chemical shift technique for studying conjugation is not normally feasible. This difficulty has been overcome in a very novel way by the use of suitably chosen sterically hindered derivatives. A prliminary study of 4- and 5-substituted *o*-nitrobenzoic esters, suggested that hyperconjugation is quite significant in the ground states of such molecules. This method has now been amplified and extended so that its full potential could be exploited.

A series of substituted phthalic esters have been examined and the characteristic variation of chemical shifts with donor-acceptor interaction in such systems has been illustrated. A comparison of the methyl and *t*-butyl derivatives have again shown that the indication with regard to hyperconjugation is positive. The absorptions of the carbomethoxyl groups are resolved in almost all of these compounds and one of them exhibits remarkable bandwidth changes with concentration. It could be recognized that the donor strength of the substituent is one of the factors determining the separation between the methoxyl signals. In an attempt to estimate the influence of the steric factor on the aromatic proton chemical shifts several anilinium and aryltrimethyl ammonium salts have been studied. The data obtained are interesting; but they are yet to be fully evaluated.

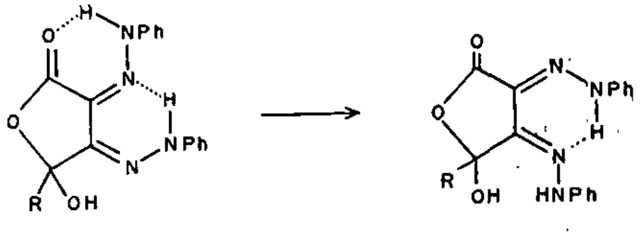
Parallel studies on three series of derivatives of *o*-dinitrobenzene and *o*-nitrobenzoic acid have been undertaken and substantial preparative progress has been made.

Vibrational band intensities : In an attempt to obtain supporting evidence for the tentative conclusions of the chemical shift study mentioned above, infrared intensity measurements have been made on the C = C stretching (γ_{16}) bands of two series of substituted benzoic and phthalic esters and the NO_2 symmetric stretching bands of a few nitro compounds. The results obtained have been very helpful and their detailed interpretation is under consideration. The variation of the frequencies of the γ_{16} vibrational mode is also of considerable interest.

11·3 *Structural and stereochemical studies* : (B-5.6/67)

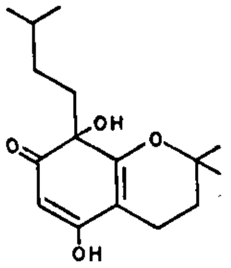
Osazones of ascorbic acid and dehydroascorbic acid : The structures of the osazone-like derivatives obtained from ascorbic acid and dehydroascorbic acid have never been investigated. The nature of the products obtained appearently depended on the method of preparation. The reports are confusing and contradictory as regards the identity of the products.

A systematic study of the structures of these products was undertaken with the help of NMR, UV and IR spectra. It was found that the spectra in dimethylsulphoxide were time-dependent. A study of the spectral changes showed that the osazones were mutarotating in solution. This phenomenon, although well known in the case of sugar osazones has not been so far reported for ascorbic acid osazones and it has been investigated in detail. The NH protons of ascorbic acid osazone showed two pairs of signals in the NMR spectrum, one pair growing with time at the expense of the other in DMSO solutions. There were characteristic changes in other regions of the spectrum. When the transformation was followed with the help of IR spectra it was found that a hydrogen bonded C = O group was getting converted into free C = O group. The associated shifts in UV-VIS absorption spectra were also ascertained. The structural change involved appears to be as follows :

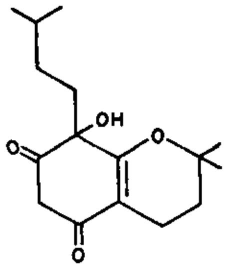


The osazone of dehydroascorbic acid obtained by iodine oxidation has also been studied. This is not identical with ascrobic acid osazone. The mutarotation of 3-*o*-methylglucosazone and L-rhamnosazone has also been studied.

The structure of " C_{16}-phenol" an unusual product from a Clemmensen reduction : The structure of a product ($C_{16}H_{24}O_4$) obtained from the alkali fusion of octahydromorellin had been investigated earlier in this laboratory and several structural features had been already recognised. A choice between the two structural possibilities arrived at from earlier work has now been made on the basis of the mass spectral fragmentation pattern, which indicates facile loss of C_5H_{10} and C_5H_{11} fragments from the molecular ion. This fragmentation is characteristic of a structure in which the C_5H_{11} side chain is on a carbon atom that is α to a carbonyl group, as well as a hydroxyl group. The structure of the product which is not a phenol is found to be, as shown in IA and IB. This compound is also formed as one of the products in the Clemmensen reduction of 5,7-dihydroxy-8-isovaleroyl-2,2-dimethylchroman-4-one. Mechanism for the formation of the C_{16} compound in the reduction as well as in the alkali fusion has been suggested.



IA (Solid)



IB (Solution)

11.4 *Studies related to the Mills-Nixon effect :* (B-5.4/62)

A recent NMR spectroscopic study has shown that the localization of π-bonds in the indane molecule is in a sense opposite to that suggested by Mills and Nixon.

Some experiments on nucleophilic reactivity in the aromatic ring were made subsequently in order to get chemical evidence for the same conclusion. Although the indications were helpful, these experiments were not adequate. In continuation of this study other derivatives (5- and 6-bromoindanols) whose nucleophilic reactivity is to be studied, have been prepared. It has also been proposed to investigate the manifestations of strain in the chemical reactivity of the alicyclic ring. Some derivatives required in this connection have been prepared.

11.5 *Carbonium ions :* (B-5.3/64)

In connection with our interest in the measurement of barriers to rotation in carbonium ions a method has recently been worked out for the preparation of a series of *p*-substituted α-acetoxybenzyl perchlorates.

The behaviour of these salts in acetic acid and acetic anhydride has been studied with the help of NMR spectra and some unexpected results have been obtained. The salts are stable in acetic acid, but they are converted into benzylidene diacetates in acetic anhydride. It has been suggested that this behaviour is related to the chemical nature of acetic anhydride. Some effort has been made to get more explicit spectroscopic evidence in this connection. The preliminary experiments have been encouraging. The study will be pursued further.

11.6 *Electronic spectra :* (B-5.9/68)

Steric and other proximity effects observable in the electronic spectra of some 16,17-disubstituted derivatives of violanthrone have been recently studied.

The spectra of some of the corresponding reductive methylation products have now given further support to the conclusions of the earlier study.

The electronic spectral evidence so far obtained in connection with hyperconjugation problem has been taken to be negative. A preliminary study of the spectra of two trisubstituted benzenes have suggested that there is a distinct possibility of getting positive evidence for hyperconjugation. It is proposed to make a detailed study in this regard.

12. MICROBIOLOGY

12.1 *National Collection of Industrial Microorganisms :* (AB-62/68)

Non-pathogenic microorganisms (yeast, becteria 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 this 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 cultures and testing of the cultures for their biochemical performance were carried out. Studies on different methods of culture maintenance were also continued. 509 cultures were sent during the year to various institutions in India and abroad. 8 cultures were added to the collection.

12.2 *Microbiological transformation of terpenes* : (B-10/59)

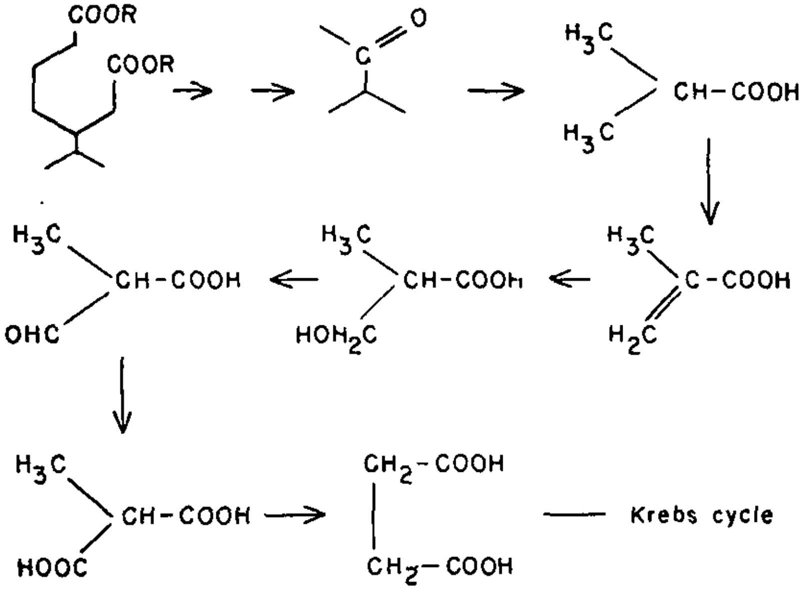
Earlier studies indicated that both fungi as well as becteria could bring about in mono- and sesquiterpenic hydrocarbons different chemical changes such as hydroxylation, hydration of a double bond, oxidation of hydroxyl groups, rupture of alicyclic rings and carbon-carbon bond cleavage. This work of fundamental interest was undertaken with a view to converting easily available terpenoid hydrocarbons into oxygenated essential oils of interest to the perfumery industry with the aid of microorganisms and to elucidating the mechanisms underlying these transformations.

12.2.1 *Bacterial transformations* :

(a) *Metabolic pathway for the degradation of β-isopropylpimelic acid* : β-Isopropylpimelic acid has been implicated as a metabolite in the bacterial degradation of α- and β-pinenes and of $\triangle^1$-*p*-menthene. Methyl isopropyl ketone has been isolated from the fermented broth when the PL-strain grows on $\triangle^1$-*p*-menthene. The isolation of this compound combined with some of the growth studies gave sufficient clue to the probable mechanism of the breakdown of β-isopropylpimelic acid to carbon dioxide and water. The organism grown on $\triangle^1$-*p*-menthene was found to grow without any lag on methyl isopropyl ketone, isobutyrate, n-butyrate, succinate, malate and acetate. $\triangle^1$-*p*-Menthene grown cells oxidised readily isobutyrate, acetate, succinate, malate, α-ketoglutarate and methacrylate, methyl malonate, methyl isopropyl ketone and β-isopropylpimelic acid were oxidized at rather slow rates.

$\triangle^1$-*p*-Menthene grown cells and isobutyrate grown cells were used under resting conditions with $\triangle^1$-*p*-menthene and isobutyrate as substrates and arsenite as an inhibitor . An analysis of the reaction products indicated the accumulation of a keto acid; the keto acid has been isolated and identified by different techniques as pyruvic acid.

Based on the growth, oxidation and resting cell experiments, a probable mechanism of breakdown has been suggested :



(b) *Fermentation of* Δ^3-*p-menthene :* The PL-strain which has been adapted to grow on Δ^3-*p*-menthene has been shown to form small amounts of menthol. The fermented broth was fractionated by conventional methods which showed the presence of a number of mono- and dicarboxylic acids. Among these a mono- and a dicarboxylic acid have been isolated in pure condition and their structures have been determined. Further work is in progress for the identification of other products.

12.3 *Transformation of Kurchi alkaloids :* (AB-34/65)

Holarrhena antidysentrica contains mainly the 18-substituted steroidal alkaloids and these have been attracting attention as potential precursors of 18-oxygenated steroids. The synthesis of 18-aldoprogesterone from conessine has already been reported. Microbiological introduction of (OH) groups at C_{11} and C_{21} positions has been carried out by the use of specific microorganisms. A hydroxyl at the 11β-position was introduced in 18-aldoprogesterone by the strain *Cunninghamella blakesleeana.* The final step in this partial synthesis is the introduction of a (OH) group at C_{21} position in 21-deoxyaldosterone to give aldosterone. This was achieved by incubating 21-deoxyaldosterone with a strain of *Ophiobolus herpotrichus.* The yield of aldosterone was about 40%. This work has been completed.

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

The study of the growth and metabolism of different plant cells is of interest to examine the formation of useful plant products. The objectives of this project at present are; (i) to determine the requirements for rapid growth of different plant cells and (ii) to study the growth of monocotyledonous cells and other plant tissues which have hitherto been investigated only to a limited extent. These studies on different plant tissues are of agricultural importance.

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

Studies on the tissue cultures of maize, jowar, rice, bajri and wheat were continued. All the cultures except bajri were viable on repeated subculture. Maize has been successfully grown under submerged conditions on rotary shaker. The rate of growth was markedly increased and the tissue consisted almost completely of roots. This is the first report of the growth of plant roots under conditions of vigorous agitation. Fifteen subcultutes have been made without any decrease in the rate of growth.' Studies on the nutritional requirements of maize, wheat, jowar and rice are being continued. A deep red pigment is produced by jowar cultures, which consists of at least twelve different components.

Several pairs of normal and tumour tissues were obtained by isolation or as a gift. A comparative study of the metabolism of normal and tumour cells and the effect of anti-tumour compounds is being carried out. Work on improving the cloning efficiency of plant cells and increasing their growth rate is also being continued.

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 for the solubilization of particulate hexokinase of brain and heart was discovered. The enzyme from brain was purified till it was 90 per cent pure as shown by ultracentrifugal studies.

Studies on the kinetics and properties of brain hexokinase were completed. The substrate specificity and stability of the enzyme and the effect of different metals, sulfhydryl reagents and other compounds on hexokinase were determined. A detailed study was made of the inhibition of the enzyme by glucose-6-phosphate and the reversal of the inhibition by Pi and the effect of different compounds on hexokinase activity in the presence of glucose-6-phosphate and Pi. The insoluble hexokinase of heart has also been purified about 500-fold. Glucose-6-phosphatase of liver, which has hexokinase activity with glucose and pyrophosphate, has also been obtained in a stable and soluble form. It was found to have a molecular weight of about 300,000.

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.

Further purification of the enzyme by fractionation on IRP-64 and DEAE-cellulose was carried out. The induction of the enzyme in diffrrent cultures of *B. subtilis* was also 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 was solubilized by two independent methods and purified about 40-fold. Its molecular weight by the use of Sephadex G-200 was found to be approximately 80,000. Phosphate was found necessary for the stability of the enzyme.

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.

The enzyme was purified 5000-fold to yield a stable preparation with a specific activity of 100,000 units/mg. Detailed studies on its kinetics and properties were carried out. It has a broad pH optimum between 7.5 and 8.5. The K_m values at different pHs and temperatures and Ki for fluoride, butyrylcholine, eserine and prostigmine were determined. Prostigmine inhibition was pH-independent whereas inhibition by eserine decreased with increase in pH. The molecular weight of the enzyme was found to be approximately 200,000 by gel filtration. Studies on the unusual observation that the enzyme is inactivated when it is frozen in the presence of phosphate and thioethanol were continued.

14.5 *Acylphosphatase :* (B-12.7/68)

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

Acylphosphatase was found to occur in several plant tissues and in a culture of tumour tissue. After partial purification the enzyme was shown to be a true acylphosphatase and different from an ATPase and a non-specific phosphatase present in the tissues. The acylphosphatase was purified about 1000-fold.

14.6 *Citrate-oxaloacetate lyase* (*Citrase*) *:* (B-12.5/65)

The subunit structure of the enzyme has been determined and the conditions for the dissociation of the molecule into subunits in three distinct stages have been established. The subunit structure of the enzyme in the presence of reagents such as urea, guanidine hydrochloride and sulphhydryl reagents has been studied.

The induction of the enzyme in spheroplast preparations of the organism has been demonstrated in presence of citrate. A series of related organic acids which were tested had no effect as inducers. Trials are in progress to design a sensitive immunological assay for enzyme induction.

14.7 *Enzymes and the metabolism of organic acids* : (B-12.8/68)

The objective has been to study the biosynthesis and biodegradation of uncommon organic acids and the mechanism of action of some of the enzymes concerned with this.

Studies on the metabolism of (–) -citramalate and maleate have continued. DL-citramalate-1-^{14}C and DL-citramalate-2-^{14}C have been chemically synthesized for this purpose. Separation and identification of the intermediates in the degradation of citramalate are in progress.

The enzyme malease present in bacteria (grown on either maleate or citraconate) has been found to be rather unstable. The product of the malease-catalyzed hydration of maleate has been proved to be D (+) -malic acid on the basis of chemical, physical and enzymatic data.

The work on the purification of citraconase has been brought to a stage and temporarily stopped. The results of studies on purification and properties of this enzyme have been communicated for publication.

A bacterium grown on DL-malic acid forms three enzymes for the dehydronation of malate : two L-malate dehydrogenases and one D-malate dehydrogenase. D-malate dehydrogenase and one of the L-malate dehydrogenase appear to be different from what are known now. These enzymes are being studied.

14.8 *Nitrate and nitrite reductases :* (B-12.6/64)

Microorganisms play an important rôle in maintaining the nitrogen cycle. The activity of denitrifying bacteria accounts for substantial losses of nitrate-containing fertilizers. Biochemical studies undertaken with whole cells will help understand the basic mechanisms involved in these denitrifications. Thus the study has a bearing on understanding soil fertility itself.

Ultracentrifugally homogeneous nitrite reductase from *A. fischeri* was found to catalyze the reduction of hydroxylamine also. Studies on kinetics, optimum pH and the effect of different inhibitors on hydroxylamine reduction were completed. The initial-rate concentration data obtained for nitrite and hydroxylamine reductions obey normal Michaelis-Menten kinetics and do not change in form in or value with variations in pH. Data obtained suggest that nitrite and hydroxylamine reductase activities are properties of the same enzyme and that both nitrite and hydroxylamine are reduced at a common catalytic site.

Preliminary observations with whole cells indicated that the product of nitrite reduction is nitric oxide.

There is evidence that nitrite reductase is dissociated into subunits. Work on the subunit nature by physico-chemical methods, the kinetics of the reformation of the acid-inactivated enzyme, determination of heme and iron will be continued.

Attempts to establish conditions for the synthesis of nitrate and nitrite reductases in a cell-free system were unsuccessful.

15. PHYSICO-CHEMICAL STUDIES ON POLYMERS

15.1 *Stereospecific polymerization :* (B-13.1/60)

Earlier it was reported that high molecular weight syndiotactic polymethyl methacrylate was obtained when polymerization was carried out with $VOCl_3$-Al(C_2H_5)$_3$ system at 40°. This had been hitherto possible only at temperatures below 0°.

A kinetic study of the polymerization of this system, using Al/V ratio of 1:5 and aging time of 20 minutes, showed that the rate of polymerization as well as molecular weight increased during the first two hours and then decreased. The decrease could be due to covering of the catalyst sites with the precipitated polymer in n-hexane. A first order reaction was found in respect of both monomer and catalyst concentration, and values of the estimated rate constants as well as of the overall activated energy were of the order usually observed with Ziegler catalysts. Furthermore, there was no change of colour with the addition of increasing quantities of DPPH (diphenyl picryl hydrate inhibitor) and the rate of polymerization decreased only slightly, thereby ruling out the possibility of a free radical mechanism of polymerization. It was also found that the addition of small quantities of certain electron donating compounds such as pyridine and triethylamine to the system prior to the addition of monomer led to increase of molecular weight and percentage conversion up to a certain ratio (of electron donor/vanadium) and thereafter decreased. The increase is attributed to site activation by the adsorption of amine (donor) on the uncoordinated active sites, whereas, subsequent decrease is due to excees adsorption and consequent non-availability of active sites (as a result of coordination).

It is further proposed to study the polymerization using VCl_4–Al (C_2H_5)$_3$ as the catalyst.

15.2 *Polymerization of ω-aminoenanthic acid :* (B-13.3/68)

Experimental work to study the effect of temperature and time on the polymerization of ω-aminoenanthic acid (leading to polymer Nylon-7), using a few acidic and alkaline catalysts, has been carried out. The polymers obtained have been fractionated and characterized for their molecular weight by using the end-group method as well as by viscometry. Molecular weight distribution curves have been drawn and further work is in progress.

15.3 *Degradation of long chain molecules by ultrasonics :* (B-13.3/63)

The study of the degradation of polymers is of great interest both in its fundamental and applied aspects. 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 rubber (trans rubber) have been studied. The rubber has been fractionated into several fractions and molecular weight for five fractions have been determined by light scattering method employing Zimm's plot. For kinetic analysis, a previous knowledge of the relationship between molecular weight and viscosity for neoprene in different solvents was necessary, and this has been evaluated at 30° as $[\eta] = 4.607 \times 10^{-4} \times M^{0.625}$ and $6.301 \times 10^{-4} \times M^{0.587}$ in chloroform and toluene respectively.

16. CHEMICAL ENGINEERING STUDIES

16.1 *Interfacial tension in two and three component systems :* (B-14.1/66)

Correlation and prediction of liquid-liquid interfacial tension in heterogeneous liquid systems is of considerable importance. Relatively little work has been reported on such non-aqueous systems. Six binary systems with glycerol as one common component and four others with diethylene glycol (2-2-dihydroxyethyl ether) as another common component were studied; the former six systems at different temperatures between 30-50°. The drop-volume method was used with all precautions recommended for it. Various reported correlations for predicting binary interfacial tension were then examined for ease and convenience of application. Deviation of calculated values (obtained from some feasible equations) from the experimental values were then determined to calculate errors. Some selected binary equations were also tested with about 100 values of binary aqueous data reported in literature.

16.2 *Heat transfer :* (B-14.2/66)

An experimental assembly was set up to study the performance of a packed tower in transferring heat between two directly contacted liquid phases. Data have been collected on the effect of flow-rates of the phases and the temperature of the hot oil phase regarding the efficiency of heat transfer using Raschig rings.

16.3 *Reaction models and reactor design :* (AB-40/62) (B-4.8/68)

Investigations have been completed on the dehydration of different aliphatic alcohol on Indian bauxite, and a generalized kinetic model has been developed. The constants of this model can be predicted from the bond energies and entropies of formation of the reaction components. Models have also been developed for the complex reaction system involved in the vapour-phase catalytic ethylation of aniline, oxidation of toluene (selectively to benzaldehyde) and oxidation of benzene. Interesting observations have been made on the transition from one regime of control to another. Work is in progress on a model for the isomerization of 1- and 2-betenes. Studies on the ammonolysis of methanol to methylamines are also in progress using a special type of reactor.

A model is being worked out for reaction between hydrogen chloride and ethylene in various liquid media. The necessary physicochemical data are being collected and work on the actual kinetics will commence shortly.

A model for two gases reacting in the liquid medium was proposed earlier for the formation of ethylene dichloride. This is now being extended to the formation of tetrachloroethane from acetylene and chlorine. The necessary physicochemical data have been collected. In the gas-liquid reactions, studies have been commenced on the adsorption of chlorine in solutions of different substances having a double bond and the mechanism of these reactions is being investigated. This last part is being done in collaboration with the Department of Chemical Technology, Bombay.

16.4 *Properties estimation :* (AB-41/62) (B-14.12/68)

During the period under review estimation procedures have been worked out for entropy of formation, latent heat of vaporization and surface tension. A new method has been proposed for estimating the Prandtl number. Experimental assemblies have also been set up for determining some thermodynamic properties.

16.5 *Mass transfer :* (AB-42/64) (B-14.6/68)

The mechanism of drop growth and mass transfer during drop formation in liquid-liquid extraction has been studied. The proposed equation, which is based on a dynamic similarity with the lines of force in a magnetic field, has been found to represent the experimental data with an average deviation of about 30%. It is now proposed to study mass transfer accompanied by chemical reaction in a dispersed drop both during the formation and steady rise periods.

Data on the flooding behaviour of pulsed and unpulsed extraction columns were obtained some time ago in this laboratory and are now being analysed in the light of several mathematical equations that have been proposed in the past and some new equations which have been developed. Over 40 mathematical models have been set up and these are being evaluated by processing the data in a computer.

16.6 *Fluidization :* (AB-43/62) (B-14.5/68)

The advantage of using an MT semi-fluidized reactor over the conventional fixed bed reactor for exothermal reactions has been demonstrated for the oxidation of benzene. It is now proposed to use this reactor for the hydrogenation of nitrobenzene, a simple reaction which can be precisely described by a single kinetic expression. Theoretical expressions for the MT and TM combinations for complex reaction systems will also be derived.

An 18″ reactor has been set up to study the stability and uniformity of the fluidized bed using a new design of reactor internals. The necessary controls for understanding the behaviour of the column have been set up. Work will soon commence on this reactor which will hold a charge of about 1/2 tonne of solid material.

Investigations are in progress on the use of the fluidized bed for heating in pilot plant as well as large scale reactors. As a first step in this study a tube-and-shell type reactor has been set up to study the fluidization characteristics.

Experimental studies are in progress on the dynamics of gas-solid-liquid beds with continuous flow of a liquid. The behaviour of such a column has been found to be quite different from the conventional slurry type of reactors in which also a gas-solid-liquid system is involved, and attempts are being made to formulate the theory of such a system.

16.7 *Diffusion in solid catalysts :* (B-14.7/68)

A cell has been designed in which the catalyst can be pressed *in situ* and a unit is being assembled to enable the determination of the effective diffusion coefficient in different catalyst pellets at pressures up to 1000 psi. One of the objectives of this study is to examine the existing diffusion models with data obtained over a wide range of pressures.

16.8 *Distillation :* (B-14.11/68)

Nomograms have been prepared for 30 equations which are used in the design of distillation columns.

A correlation has been worked out for predicting the activity coefficient from a knowledge of the physical properties of the systems involved. This correlation is expected to be further examined by using the data of two more systems.

The work on distillation is being carried out in collaboration with a private party in Bombay.

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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. *Mass spectroscopy*

During the period under review, 680 samples were analysed mass spectrometrically for structure elucidation and characterization of various naturally occurring and synthetic organic compounds.

3. *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.

2517 analyses for elements and 112 for functional groups were carried out.

4. *Spectrochemical work*

Analytical and structure elucidation work was carried out by various physico-organic techniques such as UV, IR, NMR and visible spectra.

Number of samples studied :

NMR	..	2794
UV	..	748
UV visible	..	1428
IR	..	3215

5. *VPC/GLC analysis*

5484 samples were analysed.

6. *X-ray patterns*

82 X-ray powder patterns were obtained.

7. *Ultracentrifugal analysis*

156 samples were analysed.

8. *Instrumentation*

Servicing and maintenance of the following special equipments was carried out : NMR spectrometer; IR, UV and visible spectrophotometers; X-ray machine; electrical furnaces; 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 : 365

9. *Workshop*

Special equipment fabricated :

	Item		Nos.
(i)	Variable stroke arrangement for liquid flow	..	1
(ii)	Fume extractor (Exhaust blower) Gallenkemp type	..	3
(iii)	Ice crushing machine	..	6
(iv)	Stainless steel conical percolater with stand	..	1
(v)	A unit for preparation of anhydrous aluminium chloride	..	1

Total number of jobs completed : 2778

10. *Glass blowing*

Jobs completed : 5040

5260 standard ground glass joints were fabricated.

11. *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.

Double boiled linseed oil substitute, rubber reclaiming agent, di-*o*-tolylbiguanide (Sopanox), dimethylaniline, potassium ethyl xanthate and potassium amyl xanthate, phenoxyacetic acid, phenacetin, *p*-menthane hydroperoxide, potentiometric strip-chart recorder, tri (nonylphenyl) phosphite, triethyl phosphate, staple pin adhesive, costus root oil and *p*-nitrophenol.

Terms of contract with M/s Excel Industries, Bombay, for large scale collaborative developmental work were prepared and submitted for the approval of Process Release Committee.

Economic evaluations and cost estimates were prepared for the following projects : β-Ionone, *l*-menthol, costus root oil, citronellal from lemon grass oil and ceto-stearyl alcohols.

Follow up work on the following projects which are under negotiation for their release was conducted : dihydroambrettolide, isoambrettolide, costus root oil, Sopanox, phthalates, nicotine sulphate, ethyl acetoacetate and polystyrene DVB-base cation exchange resin.

Project inputs since their commencement for various projects were calculated for the following groups in the laboratory : Physical, Inorganic, polymer, Biochemistry.

A study on the materials management set-up was undertaken.

Under the imports substitution programme, the list of imported chemicals and allied products were scrutinized and comments on each of the item as to whether NCL is willing to undertake R & D work on the imported chemicals have been sent to the President,Indian Chemical Manufacturers Association and the ICMA- CSIR liaison centre, Bombay.

Number of charts and models were exhibited in the IITIF Exhibition, Madras, during January-February 1968. A special pamphlet giving general information on NCL and information on various NCL processes was printed and distributed.

The annual report 1966-67, half yearly report for April-September 1967 and Research Programme for 1968-69 were compiled. More than 800 enquiries from different parties were attended to and non-technical notes on various NCL processes were supplied.

Other work attended to include attending to the visitors, various enquiries from the CSIR office, government organizations and industries and collection of techno-economic data.

The division also continued rendering photographic, museological and draftsman services to other sections of the laboratory.

A-II SERVICES RENDERED TO OUTSIDE PARTIES

1. *Supply of cultures*

509 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	56	498/-
GLC analysis	17	850/-
VPC analysis	1	50/-
NMR	2	80/-
Mass spectral analysis	35	2675/-
IR	14	140/-
Ultracentrifugal analysis	2	400/-
X-ray powder pattern	8	160/-

3. *Technical aid involving ad-hoc experimental, instrumental, engineering and glass blowing services*

1. Craftsman photoelectric colorimeter repaired	Sugarcane Development Officer, Govt. of Maharashtra, Poona.
2. Servicing of Beckman zerometric pH meter, 'VIRTIS' type homogenizer, spectronic-20 colorimeter (Bausch and Lomb)	CPHERI Field Station, Poona.

3.	Klert- Summerson photoelectric colorimeter serviced	Sugarcane Research Station, Padegaon, P. O. Nira.
4.	Testing of temperature controller	Engineering College, Poona.
5.	Following glass-blowing work was carried out :	
	a. Bubbler as per sketch	Armed Forces Medical College, Poona.
	b. Repairing of carbon absorption unit	Power Cables P. Ltd., Kalyan.
	c. Ion exchange column	Indian Drugs & Pharm. Ltd., Rishikesh.
	d Fractionating column	Govt. Medicinal and Essential Oil Factory, Nilgiris.
	e. Glass equipment as per sketch	Institute of Armament Technology, Poona.
	f. Fabrication of absorption vessel, repairs of condenser and Warburg apparatus	Central Water & Power Research Station, Poona.
6.	Rice samples (15 Nos.) analysed for vitamin B_1 content	College of Agriculture, Poona.
7.	Dextran samples (2 Nos.) analysed for molecular weight determination	Unichem Laboratories Ltd., Bombay.
8.	Various samples examined by electron diffraction for the epitaxial growth	CECRI, Karaikudi.
9.	25 samples examined by electron diffraction for surface structures	NML, Jamshedpur.
10.	Phosphate sample from fungi culture analysed	RRL, Jorhat (Assam).
11.	Brass bar composition analysed	Heavy Electricals, Bhopal.
12.	Silica sample analysed	M/s Merck, Sharp & Dome, Bombay.

13. Six trial samples of iron oxide catalyst supplied	M/s Polychem Ltd., Bombay.
14. Iron oxide samples (of certain specifications) prepared from ferrous sulphate and supplied	M/s B. D. H. Ltd., Bombay.
15. Flux composition for the soft soldering of aluminium supplied	M/s Binani Metal works, Calcutta.
16. Capacities of few ion-exchange resin samples measured	Bombay Municipal Corporation, Bombay.
17. Samples of polycaprolactum powder for chromatography supplied	CDRI, Lucknow.
18. Seven samples of mucilages analysed for viscosity	NBG, Lucknow.

A-III DEMONSTRATIONS

Manufacturing of styrene DVB- base cation exchange resin (improved process)	M/s. Industrial & Agricultural Engg. Co., Bombay.
Fabrication and building of VPC unit	M/s Associated Instruments Manufacturers (India) P. Ltd., New Delhi.
Process for the manufacture of aniline	M/s Hindustan Organic Chemicals Ltd., Panvel. M/s Engineers India Ltd., New Delhi.
Preparation of dioctyl and dibutyl phthalates	M/s R. L. Dalal & Co., Bombay.

A-IV PROCESSES LEASED OUT DURING 1967-68

Process	*Party*	*Remarks*
Dimethyl and diethyl phthalates	M/s Mysore Acetate & Chemical Co. Ltd., Bangalore.	Non-exclusive

Sisal wax	M/s Deccan Paints & Chemical Industries, Saikla, Hawrah.	Non-exclusive

A-V SPONSORED PROJECTS COMPLETED DURING 1967-68

Rayon grade pulp from some species of woods	M/s Century Rayon, Kalyan.
Investigation of mixture of hard woods from Bastar Forest	Preinvestment Survey of Forest Resources, Ministry of Food and Agriculture, Govt. of India, New Delhi.
Benzoic acid	M/s Aniline Dyestuffs & Pharmacuticals P. Ltd., Bombay.
Improvements in the process for the manufacture of *l*-menthol from dementholised peppermint oil	M/s Bhavana Chemicals Ltd., Baroda.
Calcium hypophosphite	M/s Chunilal Ootamchand & Co., Bombay.
Calcium silicate	M/s Newkem Products Corporation, Bombay.
Nonylphenol	M/s Surfactants P. Ltd., Bombay-1.
Chlorinated copper phthalocyanine	M/s Sudarshan Chemical Industries P. Ltd., Poona-9.
Sodium cyclamate	M/s Aphali Pharmaceuticals Ltd., Ahmednagar.
Chemical investigation of ipecac root	—do—
Utilization of tung oil	U. S. Dept. of Agriculture, Washington.

A-VI TRAINING

Fifteen scientists from different universities, industries and research institutes were trained in one of the following :

Instrumental methods of analysis; techniques used in carbohydrate research and certain synthetic problems of carbohydrates; microanalytical techniques; application of IR, UV-VIS and NMR spectroscopy in organic chemistry; chemical engineering techniques; surface structure studies by electron diffraction methods; microbiological techniques, etc.

A-VII 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 the NCL.

Prof. J. W. Clark-Jewis, Flinders University of South Australia.	(i) Hemi ketals related to pelfogynol trimethyl ether. (ii) Synthesis of some heterocyclic compounds.
Dr. P. Cohn, Chester Beathy Research Institute, London.	Composition and synthesis of ribosomal proteins.
Prof. D. C. Bradley, University of London.	NMR structural studies on polymeric metal alkoxides.
Dr. G. Narsimhan, Dept. of Chemical Engineering, IIT, Kanpur.	Stability of non-catalytic reactions and an optimum concentration progression.
Dr. M.H. Simatupang, Wood Research Institute, Hamburg.	Extractives of teak wood.
Prof. J. Chatt, F. R. S. Sussex University, U. K.	(i) Bonding in organo-transitional compounds. (ii) Stability of low valence states.
Prof. P. C. Dutta, I. A. C. S., Calcutta.	Revised structure of magnamycin.
Dr. G. T. Barnes, Dept. of Physical Chemistry, University of Queensland, Australia.	Water evaporation resistance of monolayer.

Prof. F. Zymalkowski, Director, Pharmaceutical Institute, Bonn University.	Studies of drug synthesis in the pyridine series.
Dr. Philip R. White, Roscoe B. Jackson Memorial Laboratory, Maine, USA.	(i) History of tissue cultures-Plant & animal. (ii) Nutrition of tissue cultures-Plant and animal. (ii) Tissue culture and the cancer problem. (iii) Crown gall and picea tumors-special cases. (iv) Culture parameters.

Seven NCL scientists delivered more than ten scientific lectures on different subjects at various institutes and universities in the country.

A-VIII STAFF NEWS

1. *Foreign deputations/training etc.*

Dr. K. Venkataraman attended the third symposium on 'Colour Chemistry' at Interlaken at the invitation of the Ciba Company. He also visited few research departments, institutes, universities in Switzerland, West Germany and USSR (April 1967).

Mr. A. D. Deshpande returned from France after receiving training in 'Advance techniques in the field of applied research in chemical engineering' under Indo-French Cooperation agreement (June 1967).

Dr. P. R. Subbaraman proceeded to USA for one year's post doctoral work in the University of Arizona (July 1967).

Mr. S. Gundiah returned from Japan after participation in international post-graduate university course (1966-67) held in Tokyo Institute of Technology, Japan under the auspices of Japanese Committee for UNESCO (September 1967).

Dr. K. P. Sinha attended the 'International Congress on Magnetism' at Boston, USA (September 1967).

Dr. V. G. Neurgaonkar returned from West Germany after receiving training in 'Exploitation of Indian ilmenites' under the German Academic Exchange Service of Federal Republic Germany scholarship (November 1967).

Dr. B. D. Tilak visited USSR under Indo-USSR Cultural Exchange Programme (November-December 1967).

Dr. Sukh Dev proceeded to USA as a visiting scientist, at the invitation from the Chemistry Department, Stevens Institute of Technology, New Jersey, USA (February-March 1968).

2. *Awards and honours*

Dr. S. L. Kapur received Invention Promotion Board award for his invention on 'porous rigid sand filters.'

3. *Ph.D. degrees received by NCL staff and research fellows*

Name	*University*
Mr. Bapat, B. V.	Poona
Mr. Barua, K. C.	Poona
Mr. Bhat, V. V.	Poona
Mr. Deokar, V. D.	Poona
Mr. Fairwell, T.	Poona
Mr. Ghare, D. B.	Poona
Mr. Gopakumar, P.	Poona
Mr. Gopinathan, C.	Poona
Mr. Goyal, P.	Bombay
Mr. Gupta, A. S.	Punjab
Mr. Joshi, B. N.	Bombay
Mr. Kadival, M. V.	Poona
Mr. Kamath, S. Y.	Poona
Mr. Kapadia, V. H.	Bombay
Mr. Karanjgaonkar, C. G.	Bombay
Mr. Mathur, R. K.	Bombay
Mr. Mesta, C. K.	Poona
Miss Muljiani, Z.	Bombay
Mr. Naik, B. N.	Poona
Mr. Nanavati, D. D.	Bombay
Mr. Narayanan, A.	Bombay
Mr. Neurgaonkar, R. R.	Poona

Name	*University*
Mr. Pandhare, E. D.	Poona
Mr. Pansare, V. S.	Bombay
Mr. Patil, L. J.	Poona
Mr. Patil, S. G.	Poona
Mr. Patnekar, S. G.	Poona
Mr. Phadtare, P. G.	Bombay
Mr. Prahlad, M. S.	Poona
Mr. Ramaswamy, K. K.	Bombay
Mr. Ravindranathan, T.	Bombay
Miss Rani Bai, P.	Poona
Mr. Sastry, S. D.	Poona
Mr. Seshadri, R.	Poona
Miss Shanbhag, S. N.	Poona
Mrs. Siscovic, E.	Poona
Mr. Siscovic, N.	Bombay
Mr. Sobti, R.R.	Bombay
Mr. Subba Rao, H. K.	Poona
Mr. Subramanian, S. S.	Madras
Mr. Thankarajan, N.	Poona
Mr. Vaidyanathan, K.	Bombay
Mr. Venkateswaran, P. R.	Bombay
Mr. Wadia, M. S.	Poona

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.	Sri 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, N. D.	Poona, Bombay, Shivaji.
Dr. Goswami, A.	Calcutta, Poona, Punjab.
Dr. Gupta, J.	Bombay, Poona, Punjab, Madras.
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.
Dr. Nair, P. M.	Poona, Shivaji, Andhra.
Dr. Pai, M. U.	Bombay.
Dr. Pant, L. M.	Poona.
Dr. Rao, A. S.	Poona, Bombay.
Dr. Rao. M. R. R.	Bombay, Poona.
Dr. Sadana, J. C.	Poona.
Dr. Sen, D. N.	Poona, Bombay.
Dr. Sinha, A. P. B.	Poona, Banaras, Vikram, Karnatak.
Dr. Sinha, K. P.	Poona, Agra, Bombay.
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.

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A-X PATENTS IN FORCE

Patents sealed

1. **45666**

   Manufacture of nicotine sulphate from tobacco waste.
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2. **47439**

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3. **54867**

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5. **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.

6. **57888**

   Improvements in or relating to the production of hydroxy, alkoxy or aryloxy substituted aryl alkyl ketones.
   Bose, J. L. and Shah, R.C.

7. **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.

8. **59419**

   A process for the preparation of tridecane 1:13 dicarboxylic acid or its ester, suitable for the preparation of exaltone (cylopentadecanone).
   Ghatge, B. B., Nayak, U. G., Chakravarti, K. K. and Bhattacharyya, S.C.

9. **59497**

Production of porous polymer suitable for preparing cation exchange resins.
Govindan, K. P., Pandya, R. N. and Krishnaswamy, N.

10. **59606**

Preparation of cation exchange resin from porous cashewnut shell liquid polymer.
Krishnaswamy, N., Pandya, R. N. and Govindan, K. P.

11. **59608**

Rigid filters.
Kapur, S. L. and Pandya, R. N.

12. **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.

13. **60555**

Production of liquid rubber.
Uma Shankar.

14. **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.

15. **62890**

A new process for the production of 4-hydroxycoumarin and its derivatives.
Shah, V. R., Bose, J. L. and Shah, R. C.

16. **63083**

A new method for the preparation of 4-hydroxycoumarins.
Shah, V. R., Bose, J. L. and Shah, R.C.

17. **64958**

Improvements in or relating to polishing compositions.
Shah, S. M., Hinge, V. K., Mhaskar, V. V. and Shah, R.C.

18. **65440**

A process for the extraction of wax from sisal waste.
Shah, S. M., Hinge, V. K., Mhaskar, V. V. and Shah, R.C.

19. **65543**

A process for the prepatation of ω-dicarboxylic acids and ω-hydroxy acids suitable for conversion to macrocyclic compounds.
Mathur, H. H. and Bhattacharyya, S. C.

20. **65777**

A new process for the production of 4-hydroxycarbostyrils.
Shah, V. R., Bose, J. L. and Shah, R. C.

21. **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.

22. **65976**

Improvements in or relating to suspension polymerization of vinyl monomers.
Joshi, R. M. and Kapur, S. L.

23. **65977**

Rubber-base adhesive.
Uma Shankar.

24. **66096**

A process for the production of bacterial diastase by submerged culture.
Babbar, I. J., Bekhi, R. M. and Srinivasan, M. C.

25. **66194**

Improvements in or relating to can sealing composition.
Raghunath, D. and Kapur, S.L.

26. **66803**

Improvements in or relating to the manufacture of pressure sensitive adhesive tapes.
Kapur, S. L. and Rao, B. R. K.

27. **66836**

Manufacture of ethylene dichloride.
Banerjee, S. C., Pathak, S. L., Pai, M. U. and Doraiswamy, L. K.

28. **66966**

An improved process for the manufacture of porous rigid filters.
Kapur, S. L. and Pandya, R. N.

29. **67490**

Improvements in or relating to the preparation of adhesive tape.
Kapur, S. L. and Rao, B. R.K.

30. **67513**

Improvements in or relating to the separation of niobium and tantalum from each other by liquid-liquid extraction.
Sarma, B. and Gupta, J.

31. **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.

32. **71063**

Production of bacterial protease by submerged culture.
Babbar, I. J., Powar, V. K. and Jagannathan, V.

33. **71190**

Preparation of anion exchange resins.
Krishnaswamy, N., Govindan, K. P. and Dasare, B. D.

34. **72425**

A direct process for preparing the chlorides of barium and strontium from their sulphate minerals.
Iqbal, S. H., Lobo, J. and Gupta, J.

35. **73702**

A process for the preparation of cyclopentadecanolide (exaltolide).
Dhekne, V. V., Ghatge, B. B. and Bhattacharyya, S. C.

36. **74356**

Preparation of insoluble reaction products of polystyrene for use as cation exchange materials.
Govindan, K. P. and Krishnaswamy, N.

37. **74451**

Preparation of covering materials from anacardic materials.
Raghunath, D., Suryanarayana, N. P. and Krishnaswamy, N.

38. **77080**

A process for the preparation of ambrettolide.
Sabnis, S. D., Mathur, H. H. and Bhattacharyya, S. C.

39. **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.

40. **77224**

Synthetic esters as speciality lubricants for low temperature performance and particularly for the lubrication of clocks and watches.
Pathak, K. D. and Subba Rao, B. C.

41. **77225**

A process for the preparation of β-ionone from pseudoinone.
Joshi, B. N., Chakravarti, K. K., Shah, R. C. and Bhattacharyya, S.C.

42. **82189**

Production of dextro-tartaric and oxalic acids.
Vartak, H. G., Patil, S. G. and Jagannathan, V.

43. **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.

44. **83364**

Manufacture of hexachloroethane.
Bhat, N. A., Goswami, M. and Pai, M.U.

45. **83716**

Manufacture of nicotine sulphate from tobacco and tobacco wastes.
Potnis, G. V., Goswami, M., Ramachandran, V. and Pai, M. U.

46. **85446**

Preparation of carboxylic cation exchange materials.
Krishnaswamy, N., Indusekhar, V. K. and Dasare, B. D.

47. **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.

48. **86638**

A process for the preparation of 2-*iso*-propenylhexanols.
Ramaswami (Mrs.), S., Ramaswami, S. K. and Bhattacharyya, S.C.

49. **86991**

Preparation of polyurethane printing rollers.
Ghatge, N. D. and Kapur, S. L.

50. **89004**

A polycrystalline p-n junction photovoltaic solar cell.
Momin, A. U. and Sinha, A. P B.

51. **90574**

A process for the preparation of *dl*-muscone.
Nair, M. S. R., Mathur, H. H. and Bhattacharyya, S. C.

52. **90677**

A new method for the preparation of formic acid.
Vartak, H. G., Patil, S. G. and Paranjape, S. V.

53. **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.

54. **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.

55. **96663**

A new process for the manufacture of glycolic acid.
Vartak, H. G. and Patil, S. G.

56. **98156**

Preparation of solvent modified copolymers of vinyl monomers in bead form.
Kapur, S. L. and Ramkrishanan, K.

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 Bhattacharyya, S. C.

4. **96801**

A new method for the improvements in the figure of merit of thermoelectric material.
Narasimhan, K. S. V. L. and Sinha, K. P.

5. **97190**

Improvements in or relating to extractors for extraction or similar processes.
Narasimhan, G. and Shah, C. M.

6. **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.

7. **99589**

A process for the preparation of benzoyl chloride.
Aggarwal, K. L. and Doraiswamy, L. K.

8. **99590**

Process for the manufacture of a novel binding agent for core sand.
Varma, J. P.

9. **101161**

Process for the preparation of day light and pink light emitting electro-luminescent phosphors.
Ambardekar, D. S. and Biswas, A. B.

10. **106804**

Improvements related to the manufacture of carboxy methyl cellulose.
Bendale, D. S., Mahajan, M. B. and Khadilkar, H. P.

11. **106808**

Improvements in or relating to the preparation of mixed oxide ceramic compositions.
Murthy, M. N. S. and Sinha, A. P. B.

12. **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.

13. **108414**

A process for treatment of costus roots (*Saussurea lappa*) or inulin isolated therefrom for the production of fructose.
Kulkarni, G. H., Kelkar, G. R., Bose, J. L. and Bhattacharyya, S. C.

14. **109006**

A modified process for the preparation of expandable thermoplastic beads.
Kapur, S. L. and Sehra, J. C.

15. **109489**

Production of aryl-glycosides.
Ingle, T. R. and Bose, J. L.

16. **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.

17. **112575**

Thermal treatment of oil with catalyst.
Sukh Dev and Nayak, U. R.

18. **113406**

A new thermistor composition exhibiting high positive temperature coefficient of resistivity (Posistor).
Brahmecha, B. G. and Sinha, K. P.

19. **113703**

Improvements in or relating to magnesium zinc ferrites.
Krishna Rao, V. V., Kanade (Miss), S. B. and Sinha, A. P. B.

20. **113825**

110RT nickel zinc ferrites.
Krishna Rao, V. V., Kanade (Miss), S. B. and Sinha, A. P. B.

A-XI PRODUCTS MANUFACTURED ON THE BASIS OF NCL KNOW-HOW

S.No.	Name of the process and year of commencement of production	Field of utilization	Name of the manufacturer	Production and value (1967-68)	Remarks
1	2	3	4	5	6
1.	Anion exchange resin from melamine (1963)	Demineralization of liquids	M/s Tulsi Industries, Poona-13. (Hadapsar Industrial Estate)	500 cft. Rs. 1.56 lakhs	Production upto Mar. 67 50 cft.—Rs. 14,000/-
2.	Antipriming compositions (Sponsored) (1964)	Antipriming in locomotives	Research, Designs & Standards Organisation, M & C Wing, Chittaranjan.	18,700 kg. Rs. 42,500/-	Production upto Mar. 67 40,600 kg. Rs. 79,000/-
3.	Bacterial diastase (1959)	Textile desizing	M/s Chemaux P. Ltd., Mahim, Bombay-16.	Trial production	Installed capacity 750 kg./month.
4.	Berberine hydrochloride (Sponsored) (1965)	Pharmaceuticals	M/s G. Vallabhdas & Co., 180/82,Samuel Street, Bombay-9.	Trial production	300kg. —Rs. 36,000/-

1	2	3	4	5	6
5.	Calcium hypophosphite (Sponsored) (1967)	Pharmaceuticals	M/s Chunilal Ootamchand & Co., 79-F, Princess Street, Bombay-2.	250 kg. (trial production) Rs.10,000/-	20 kg. day plant installed. Estimated production will be about 6,000 kg. Rs. 2,40,000/
6.	Can sealing composition (1962)	Metal can industry	M/s Arya Chemical Works, 141/2A, Dharamtolla Street, Calcutta-13.	22,500 kg. Rs. 1.22 lakhs	Production upto Mar. 67 71,500 kg. — Rs 3,72,000/-
7.	Cation exchange resin from CNSL (1960)	Demineralization of liquids	M/s Tulsi Industries, Poona-13.	130 cft. Rs.14,500/-	Production upto Mar. 67 7,100 cft. — Rs. 5,87,000/-
8.	Chloral hydrate (Sponsored) (1963)	Industrial chemicals	Hindustan Insecticides Ltd., Industrial Area, New Delhi-15.	4,600 kg. Rs. 37,000/-	Production upto Mar. 67 7,400 kg. — Rs. 67,000/-
9.	DDT - water dispersible (1963)	Insecticides	South India Research Instt. P. Ltd., Srinagar Industrial Estate, Vijayawada-7.	400 kg. Rs.3,400/-	Production upto Mar. 67 18,800 kg. — Rs.1,27,000/-

1	2	3	4	5	6
10.	Dihydroisojasmone (1965)	Perfumery	M/s S. H. Kelkar & Co. P. Ltd., Bombay-Agra Road, Bombay-80.	40 kg. Rs.12,000/-	Experimental production.
11.	Ethylene oxide condensates (Sponsored) (1965)	Surface active agents	M/s Hico Products P. Ltd., Mogal Lane, Bombay-16.	24 tonnes Rs. 22.73 lakhs.	Production for 66-67 1,60,000 kg. — Rs. 19,24,000/-
12.	Heat sealable coating compositions (Tech. aid) (1963)	Adhesives	M/s Chandmal Fakirchand Jain, Khajuri Bazar, Indore-2.	—	Reported to be in production.
13.	Hexylresorcinol (1964)	Pharmaceuticals	M/s Unichem Laboratories Ltd., Jogeshwari, Bombay-60.	No production at present.	Production upto Mar. 67 13 kg.—Rs. 7,800/- No demand.
14.	4-Hydroxycoumarin and warfarin (1964)	Pharmaceuticals & rodenticide	—do—	10 kg. Rs. 5,400/-	Production upto Mar. 67 62 kg.—Rs. 35,000/-
15.	β-Ionone (1964)	Perfumery, pharmaceuticals	M/s S. H. Kelkar & Co. P. Ltd., Bombay-Agra Road, Bombay-80.	—	The firm is producing the item. According to them they are not producing it by NCL process.

1	2	3	4	5	6
16.	Liquid rubber (1962)	Adhesive, rubber rollers	M/s K. N. Chari &Co., 144, Nyneappa Naick Street, Madras-3.	No production at present.	Production upto Mar. 67 2,200 kg. for captive consumption.
17.	Nicotine sulphate (1963)	Insecticides	M/s Urvakunj Tobacco Bye-products, Dharmaj, Dist. Kaira.	5,000 kg. Rs. 80,000/-	Production upto Mar. 67 10,300 kg.—Rs.1,18,500/-
18.	Peach aldehyde (1965)	Perfumery	M/s S. H. Kelkar & Co. P. Ltd., Bombay-80.	300 kg. Rs. 46,700/-	Under experimental production upto March 67.
19.	Polyurethane printing rollers (1965)	Printing	M/s Saraswathy Printing Press, 32 Acharya P. C. Road, Calcutta-9.	Trial production	According to the party they are manufacturing rollers by different process.
20.	Rigid filters (1965)	Tube wells	M/s Ashim Filters,196 Defence Colony, New Delhi.	Rs. 1,71,500/-	Production upto Mar. 67 800 mtrs. — Rs. 1,34,800/-

1	2	3	4	5	6
21.	Rubber base contact adhesive (1962)	Adhesives	M/s K. N. Chari & Co., Madras-3.	3,250 litres Rs.15,500/-	Production upto Mar. 67 13,000 litres — Rs. 1,16,500/-
22.	Rubberised cork sheets (1966)	Gaskets	M/s Bharat Casements Pvt. Ltd., P. O. Box No. 89, Baroda.	6,49,600 Nos. Rs. 6.5 lakhs.	Under trial production upto March 67.
23.	Silica gel (Sponsored) (1963)	Humidity control	M/s Minco Products, 301/27,T. H. Road, Madras-21.	7,500 kg. Rs.60,000/-	Production upto Mar. 67 37,200 kg. — Rs. 1,96,000/-
24.	Sisal wax(1966)	Cosmetics, polishes	M/s Aphali Pharmaceuticals Ltd., Station Road, Ahmednagar.	—	Production upto Mar. 67 14,200 kg. — Rs. 1,53,200/- Factory is being shifted to other place.
25.	Styrene DVB-base cation exchange resin (1967)	Demineralization of liquids	Industrial & Agricultural Engg. Co. P. Ltd., 43, Forbes Street, Bombay-1.	Trial production	—

1	2	3	4	5	6
26.	Thermistors (Tech. aid) (1963)	Electronic devices	M/s Semiconductors P. Ltd. Nagar Road, Poona-14.	4,08,200 Nos. Rs. 5.97 lakhs	Production upto March 67 9,02,500 Nos.—Rs.11,80,000/
			M/s Tempo Industrial Corp., Vile Parle (E), Bombay-57.	6,000 Nos. Rs. 25,000/-	Production upto Mar. 67 2,000 Nos. — Rs. 8,000/-
Processes in production in Fine Chemicals Project:					
27.	Chromatographic alumina	Laboratory chemical		470 kg. Rs. 29,000/-	
28.	Chromatographic silica gel	Laboratory chemical		580 kg. Rs. 30,800/-	
29.	Di-*o*-tolylbiguanide	Cosmetics		450 kg. Rs.11,300/-	

A-X-II PROCESSES RELEASED AND AWAITING PRODUCTION

S.No.	Process/year of release	Field of utilization	Name of the party	Nature of licence/ proposed production/ present state of development.
1	2	3	4	5
1.	Acetanilide (1966)	Dye intermediate	M/s R. L. Dalal & Co., Hamam Street, Bombay-1 (Project Engineers).	Exclusive. Estimated production-2000 TPA by HOC, Ltd., Rasayani. Value Rs. 1 crore. Commissioning due by the end of 1968.
2.	Acriflavine (Sponsored) (1966)	Pharmaceuticals	M/s Bhaidas Karsandas & Co., 16 Appollo Street, Bombay-1.	Pre-production experiments have been conducted.
3.	Calcium silicate (Sponsored) (1967)	Low density insulation	M/s Newkem Products Corpn., Harganga Mahal, Bombay-14.	Plant under installation.
4.	Cation exchange resin polystyrene base (1965)	Demineralization of liquids	M/s Tulsi Industries, Poona-13.	Non-exclusive.

1	2	3	4	5
5.	Covering materials from CNSL (1964)	Chemically resistant flooring	M/s Natson Manufacturing Co., Bhadra, Ahmedabad.	Exclusive.
6.	Diethyl-*m*-aminophenol (Sponsored) (1966)	Dye intermediate	M/s Sahyadri Dyestuffs & Chemicals P. Ltd., Poona-9.	60 TPA capacity planned. Import licence for high pressure autoclave is pending. Production expected by Dec. 68
7.	Diethylstilbestrol (1965)	Pharmaceuticals	M/s Gluconate Ltd., 23, Camac Street, Calcutta-16.	Exclusive; 70 kg./annum.
8.	Ethyl acetoacetate (1963)	Dye intermediate	M/s Aceto Chemicals Pvt. Ltd., Calcutta-1. M/s Indian Organic Chemicals Ltd., Khopoli.	Non-exclusive. Both the licences cancelled (After April 68). —
9.	Fermentation problem (Sponsored) (1966)	Pharmaceuticals	M/s Aphali Pharmaceuticals Ltd., Ahmednagar.	This problem was of trouble - shooting type, which has been successfully completed.
10.	*l*-menthol from dementholised peppermint oil (1967)	Fine chemicals and drugs	M/s Bhavana Chemicals Ltd., Laxmi Insurance Bldg., Bombay-1.	Project was for improving the existing process. Machinery is being installed.

1	2	3	4	5
11.	Opium alkaloids (1966)	Pharmaceuticals	Govt. of India, Ministry of Finance, New Delhi.	Exclusive; 4.7 TPA—value Rs. 1 crore. Detailed designs of civil, mechanical and electrical works completed.
12.	Phthalates-dioctyl and dibutyl (1966)	Plasticizers	M/s R. L. Dalal & Co., Bombay-1 (Project Engineers)	Non-exclusive. Firm is offering 1,500 to 10,000 TPA plants to different parties; under negotiation.
13.	Phthalates-diethyl and dimethyl (1968)	Plasticizers	M/s Mysore Acetate & Chemicals Co. Ltd., Sri J. W. Road, Bangalore-2.	Non-exclusive. Detailed process designs supplied in March 1968.
14.	Studies in pine oil (Sponsored) (1966)	Industrial chemicals	M/s Prabhat General Agency, 105, Kalbadevi Road, Bombay-2.	The project was of testing nature.
15.	Thiodiglycol (Sponsored) (1961)	Dyestuffs	M/s Hico Products Pvt. Ltd. Bombay-16.	Not producing for economic reasons.

1	2	3	4	5
16.	Titanium tetrachloride (Sponsored) (1967)	Industrial chemical for the manufacture of TiO_2	M/s Travancore Titanium Products Ltd., Trivandrum-7.	Capacity 150 TPA—Rs. 4,50,000/- Pilot plant being installed.
17	Vitamin C (1966)	Pharmaceuticals	Hindustan Antibiotics Ltd., Pimpri, Poona.	Exclusive; 125 TPA plant envisaged. Foreign exchange for the plant is not yet released.

Following processes which have been mentioned under the Table I are also licensed to the following additional firms.

1	2	3	4	5
18.	DDT—water dispersible (1967)	Insecticides	M/s Lotus Industries, 62/20, Luz Church Rd., Madras-4.	DDT allotment has been done, production will commence soon.
19.	Liquid rubber (1962)	Adhesives	M/s Swastik Rubber Products Ltd., Poona-3.	No production for want of demand
20.	Nicotine sulphate (1963)	Insecticides	M/s National Tabacco By-products, Dal Mandi, Saharanpur. M/s Tobacco By-products P. Ltd., Fort Narasarowpet, Guntur.	Non-exclusive on territorial basis.

1	2	3	4	5
21.	Polyurethane printing rollers (1965)	Printing	M/s United Ink & Varnish Co., Bombay-57.	Import license for chemicals pending.
			M/s Dabholkar Brothers, Poona-1.	—
22.	Sisal wax (1966)	Cosmetics, polishes	M/s Shalimar Rope Works, 14, Netaji Subhash Rd., Calcutta.	—
			M/s Deccan Paint & Chemical Industries, 298 G. T. Rd., North Calcutta.	—
			M/s Industrial & Engg. Corporation, 84-B Bondel Rd., Calcutta.	—
23.	Styrene-DVB cation exchange resin (1963)	Dimeralization of liquids	M/s Tulsi Industries, Poona-13.	This firm claims that it is producing the resin by a different process. Chemicals are being imported.
			M/s Bird & Co. Ltd. Chartered Bank Bldg., Calcutta-1.	
24.	Thermistors (1963)	Electronic devices	M/s Adept Laboratories, Karve Rd., Poona-4.	—

A-XIII 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 composition	Already in production.
3.	Cation exchange resin (swelling type)	Licensed to one firm; production awaited.
4.	Dihydroisojasmone and peach aldehyde (technical aid to industry)	Already in production.
5.	Heat sealable coating composition (technical aid to industry)	Already in production.
6.	β-Ionone	Under negotiation.
7.	Liquid rubber	Production for captive use.
8.	Nicotine sulphate	Available for exploitation in Southern and Eastern zones.
9.	Polyurethane printing rollers	Under experimental production. Licensed to three parties.
10.	Phthalates-diethyl and dimethyl	Released to one firm.
11.	Phthalates-dioctyl and dibutyl	Turn-key plants are offered through project engineers.
12.	Rubber base contact adhesive	Already in production.
13.	Rubberised cork sheets	In production.
14.	Silica gel (desiccant type)	In production.
15.	Sisal wax	Licensed to four firms.
16.	Thermistors (technical aid to industry)	Licensed to three firms; two in production.
17.	DDT - water dispersible	Licensed to two firms; one in production.

(B) KNOW-HOW AVAILABLE ON PILOT PLANT SCALE

S. No.	Process	Batch size
1.	Aniline (offered through project engineers only)	5 kg./hr. continuous
2.	BON acid	3 kg./batch
3.	Costus root oil	1 kg./batch
4.	Dimethylaniline (Turn-key plants offered through project engineers only)	9 kg./batch
5.	* Di-*o*-tolylbiguanide (Sopanox)	50 kg./batch
6.	2, 4-Dinitromonomethylaniline	50 kg./batch
7.	Ethylene dichloride	3 kg./hr. continuous
8.	Hexachloroethane	10 kg./hr.
9.	Modified sugarcane wax	5 kg./batch
10.	Monoethylaniline	8-10 kg./hr. continuous
11.	Phenacetin from *p*-phenetidine	50 kg./batch
12.	* Phenoxyacetic acid	50 kg./batch
13.	* Rubber reclaiming agent	20 kg./batch
14.	Sorbitol	10 kg./batch
15.	Styrene DVB-base anion exchange resin	15 kg./batch
16.	Substitute for double boiled linseed oil	100 kg./batch

* Release of these processes is under negotiation.

(C) PROCESSES WORKED OUT ON LABORATORY SCALE AND TO BE WORKED ON PILOT PLANT SCALE

1. Carbon tetrachloride and chloroform from methane
2. Chlorides of barium and strontium
3. Diethyl-*m*-toluamide
4. Ethylene diamine
5. Lanolin from wool grease
6. Luminescent materials
7. Monoethylaniline
8. N. P. Fertilizers
9. Raney alloy
10. Saponin from soapnuts
11. Silicon intermediates
12. Silicon tetrachloride
13. Steroids from sugarcane wax
14. Substitute for gum Arabic
15. Triethyl phosphate
16. Tri (nonylphenyl) phosphite (Polygard)
17. Vanadium pentoxide catalyst

(D) KNOW-HOW AVAILABLE ON LAB. / BENCH SCALE

1. Cadmium sulphide photo-conductive cells
2. Civetone
3. Coating for oil filter papers
4. * Dihydroambrettolide and Isoambrettolide
5. Dihydrocivetone
6. Dithranol
7. Exaltolide
8. Exaltone
9. Hard ferrites
10. 4-Hydroxycarbostyrils
11. Isocyanate-based adhesive
12. *dl*-Menthol from citronellal
13. Neo-lavandulol
14. *p*-Nitrophenol
15. **p*-Menthane hydroperoxide
16. Potassium ethyl xanthate
17. Sealants for canvas water bages
18. Soft ferrites
19. Staple pin adhesive
20. Styrenated alkyds
21. Typewriter rollers

Instruments

1. Potentiometric strip chart recorder

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* Release of these processes is under negotiation.

ADDENDUM

SPONSORED PROJECTS

Manufacture of malathion, phorate, pentachlorophenol and other chlorophenolic compounds : (SP-8/67)

Bench scale studies of the preparation of pentachlorophenol and 4,6-dichloro-*o*-cresol were completed and further scaling up work for the former is in progress. Preparations of *p*-chloro-*m*-xylenol and dichloro-*m*-xylenol, used as general antiseptics, were carried out on laboratory scale.

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