ANNUAL REPORT

1970-71

National Chemical Laboratory, Poona

NATIONAL CHEMICAL LABORATORY
POONA
1970-1971

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

INTRODUCTION

This report describes the progress made by the National Chemical Laboratory (NCL) during the period April 1970-March 1971. The activities of the laboratory are presented under five sections: sponsored projects, pilot plant projects, product oriented research, research projects and infrastructure activities including services rendered to outside organizations. Information regarding projects completed the period (sponsored and regular), training, seminars and lectures, staff news, consultancy, publications and patents, staff strength and cost/benefit analysis is given in Appendices at the end of the Report.

INDUSTRIAL PRODUCTION BASED ON NCL KNOW-HOW

The achievements of NCL as regards contributions to industrial research and production are presented in a tabular form (Table I, page 124) wherein information on production of various products which have been commercialized on the basis of NCL know-how is given. Table II (A & B pages 135-140) lists processes which are awaiting commercial production.

When a process/product developed in a research and development organization is utilized for commercial production it helps to increase the Gross National Product of the country. Thus contributions of research laboratories engaged in industrial research should be reflected in the total sales turnover/economy achieved as a result of the successful commercial exploitation of the processes developed by such research organizations.

Performance of the NCL when judged by the above criteria shows that the Laboratory is making valuable contributions to the Indian chemical industry The data on commercial production based on NCL know-how obtained from users of NCL technology given in Table I shows that the Laboratory is showing excellent progress. Thus there has been almost an exponential increase in the value of such commercial production during the last three years. Whereas the value of production of 47 products/processes in 1968-69 was Rs. 70 lakhs and in 1969-70 for 53 products/processes it was Rs. 130 lakhs, the value of production during 1970-71 was more than two fold having reached Rs, 284 lakhs for 55 products/processes.

In Table II (page 135) information is given on 28 more processes which have been released and are expected to go into production in the near future. It may be seen that in the list of 55 processes described in Table I, items such as - acetanilide, phthalates, ethylene oxide condensates etc. contribute most to the turnover. These products have been introduced in the last 2-3 years and even these plants have yet to reach full capacity. In addition production of the following bulk industrial organic chemicals based on know-how developed at the NCL is expected to be established in the course of the next 2-3 years: Vitamin C, chlorobenzenes, *p*-nitrophenol, opium alkaloids, aniline, dimethylaniline and chloromethanes. It may therefore be expected that the value of production based on the NCL know-how in the coming years is likely to be substantially higher than the year under review.

Some of the significant achievements of the laboratory in transfer of its technology to industry are cited below :

(i) M/s. India Carbon Ltd., Bombay, established commercial production of dioctyl phthalate, an important plasticizer. The production for only two months (February and March 1971) was 318 tonnes valued at Rs. 24·2 lakhs.

(ii) Commercial production of the following additional 6 items has been established during the period: Carbimazole (10 kg; Rs. 83,000) by M/s. Indian Schering Ltd., Bombay (a sponsored project); Diethyl-m-aminophenol (4 tonnes, Rs. 2·4 lakhs) by M/s Sahyadri Dyestuffs & Chemicals (P) Ltd., Poona (a sponsored project); Geraniol & other compounds (2 tonnes, Rs. 2·6 lakhs) by M/s Radhakisan Rajaram & Co, Bombay (a sponsored project); Diethyl phthalates (48 tonnes, Rs. 3·72 lakhs) by M/s Mysore Acetate & Chemicals, Bangalore; CdS photoconductive cells (Rs. 50,000) by M/s. Gera Engineering Co., Poona; orthotolyl biguanide (2·8 tonnes, Rs. 74,000) by M/s Industrial Perfumes Ltd., Bombay.

(iii) After successfully operating the experimental unit based on NCL know-how for the chlorination of methane in a fluidized bed reactor, a semi-commercial pilot plant (300 TPA capacity for carbon tetrachloride and chloroform) designed by the laboratory has been established by the firm. This pilot plant was recently commissioned successfully by M/s. Standard Mills Ltd. Bombay, with the assistance of NCL Staff. Photographs of the above semi-commercial plant appear elsewhere in the report. The above firm hopes to put up a 3000 TPA plant for manufacture of these chemicals in active collaboration with the NCL.

KNOW-HOW AVAILABLE

Tables III and IV on pages 141-148 enlist more than 70 processes for which know-how is available from the NCL. These processes cover a wide range of chemical products of commercial importance including industrial chemicals, dyes and drugs, intermediates, pharmaceuticals, perfumery and fine chemicals etc.

SPONSORED PROJECTS

During the year work on 10 sponsored projects has been concluded and work on 14 new projects was undertaken. Currently work on 27 sponsored projects is in progress, of these 19 are sponsored by industry 6 by State and Central Govt. agencies and 2 are being supported by PL-480 grants. The receipts on account of sponsored projects for 1970-71 amounted to Rs. 6·68 lakhs.

PILOT PLANT PROJECTS

Four pilot plant projects were operated during 1970-71. The fine chemicals unit has made a profit of Rs. 0·23 lakhs for the second consecutive year.

PRODUCT ORIENTED RESEARCH

Of the 69 product oriented projects, 9 relate to solid state materials, 8 to industrial inorganic chemicals, 37 to organic fine and bulk chemicals, 10 to industrial polymers and 5 to instruments.

BASIC RESEARCH

Report on basic work, presented in the section titled 'Research projects' relates to various fields such as, solid state, thin films, nuclear and radiation chemistry, thermodynamics, transport properties, synthetic inorganic chemistry, physico analytical chemistry, natural organic products, synthetic organic chemistry, polymer chemistry and chemical engineering studies. Results of the above and other work have been published in 90 research papers. 7 scientists (2 research fellows) received Ph. D. degrees.

COST/BENEFIT ANALYSIS

Appendix XI on page 150 gives the cost/benefit analysis of the NCL for the year under review. Since the last Annual Report, we have been giving data on the recurring and capital expenditure of the laboratory (inputs) as against direct receipts and indirect benefits for which the laboratory can rightfully claim due credit.

In 1969-70 the total expenditure on the NCL was Rs. 71·57 lakhs comprising of Rs. 64·40 lakhs by CSIR and Rs. 7·1 lakhs on account of sponsored research, whereas direct receipts were Rs. 14·72 lakhs. For the year under review the total recurring and capital expenditure was Rs. 82·43 lakhs whereas direct receipts amounted to 15·01 lakhs. Of the above total expenduture, inputs by CSIR were Rs. 75·75 lakhs and the remaining Rs. 6·68 lakhs was on account of sponsored projects.

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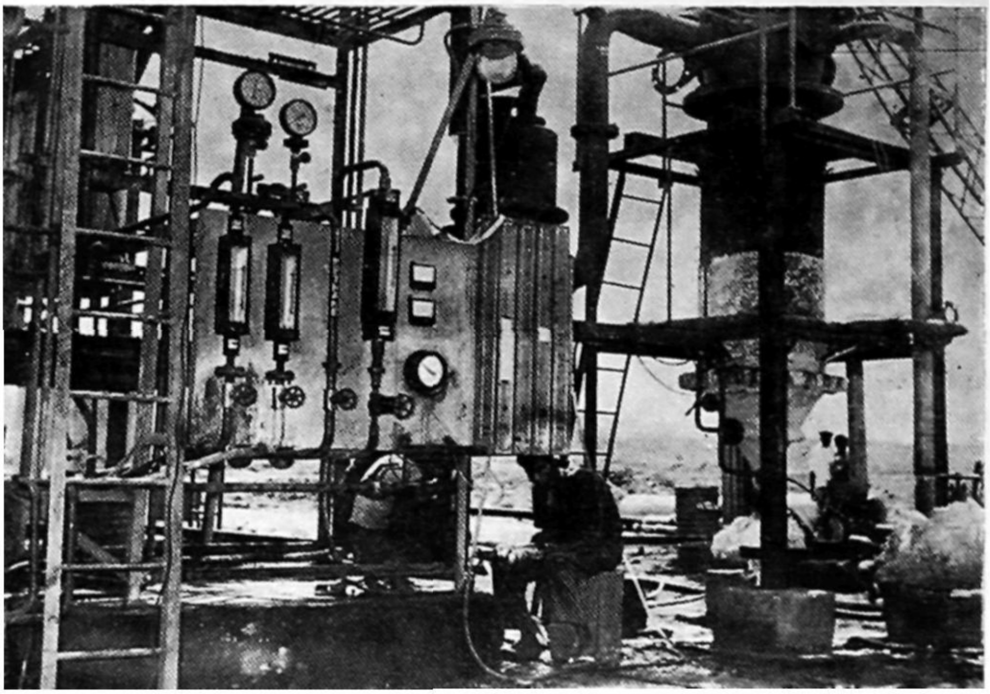
M/s Standard Mills Co. Ltd., (Chemicals Div.) Thana, Bombay.



Integrated pilot plant for carbon tetrachloride and chloroform (Capacity 300 TPA) -
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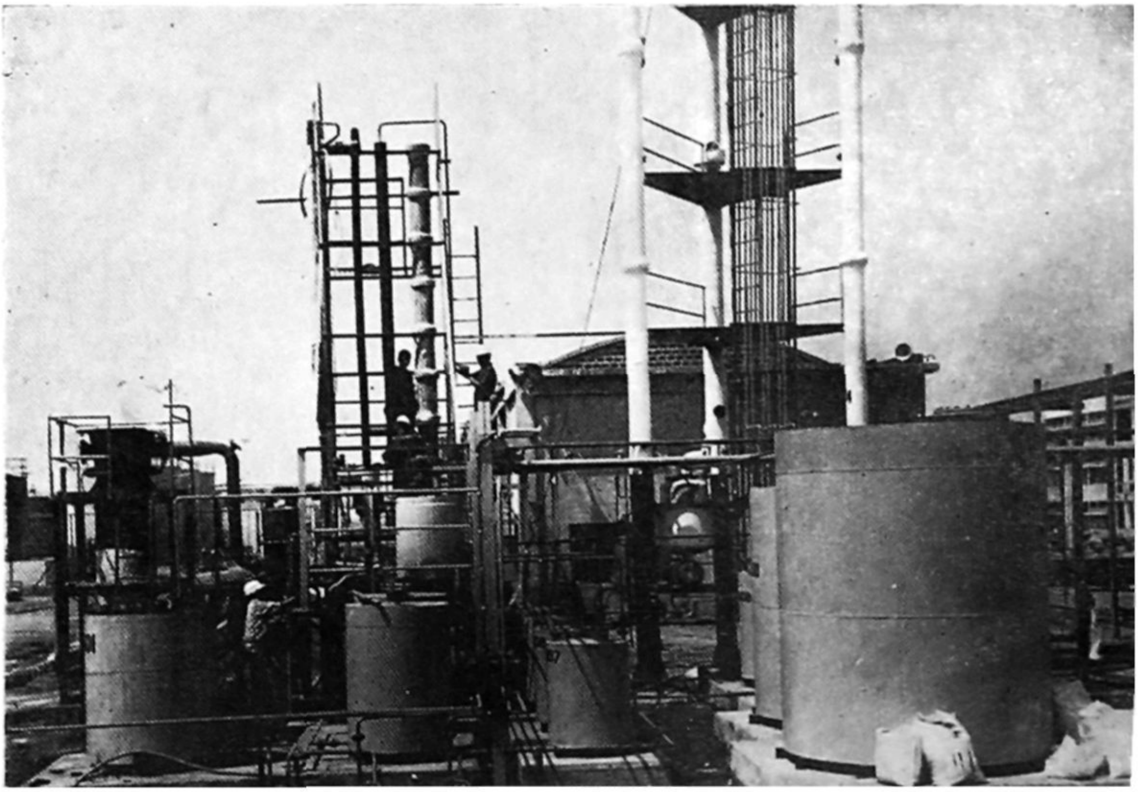

Fractional distillation columns
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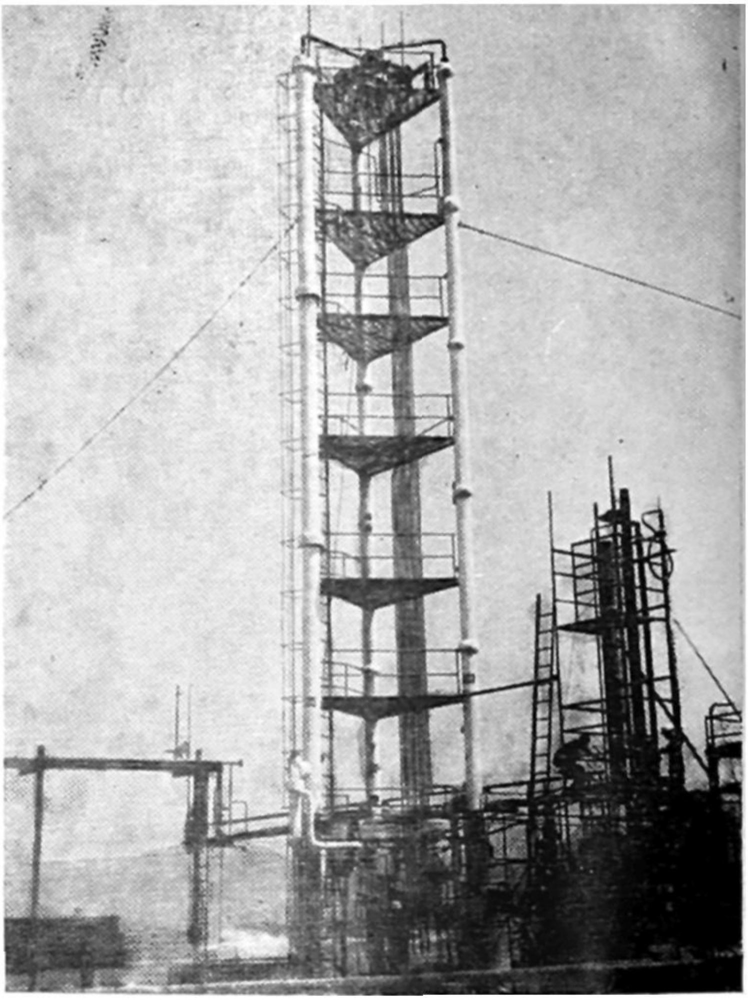
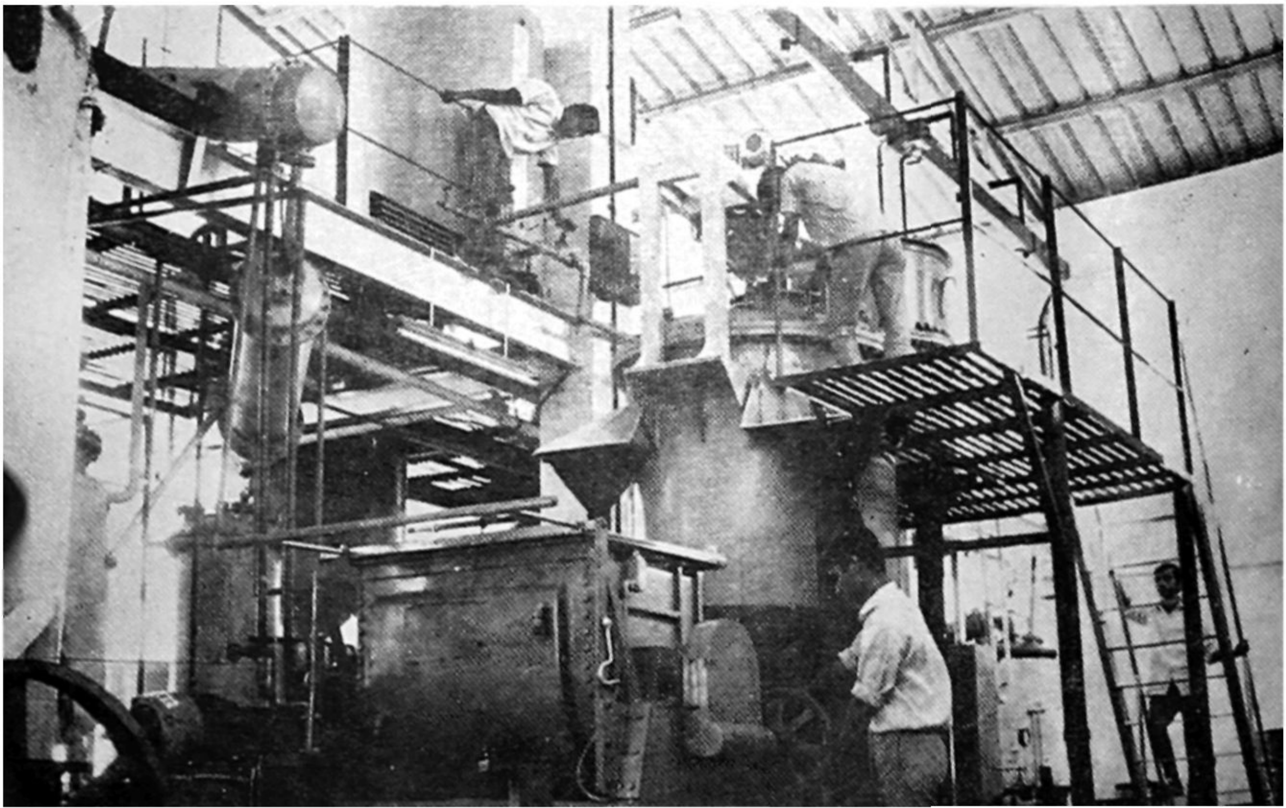
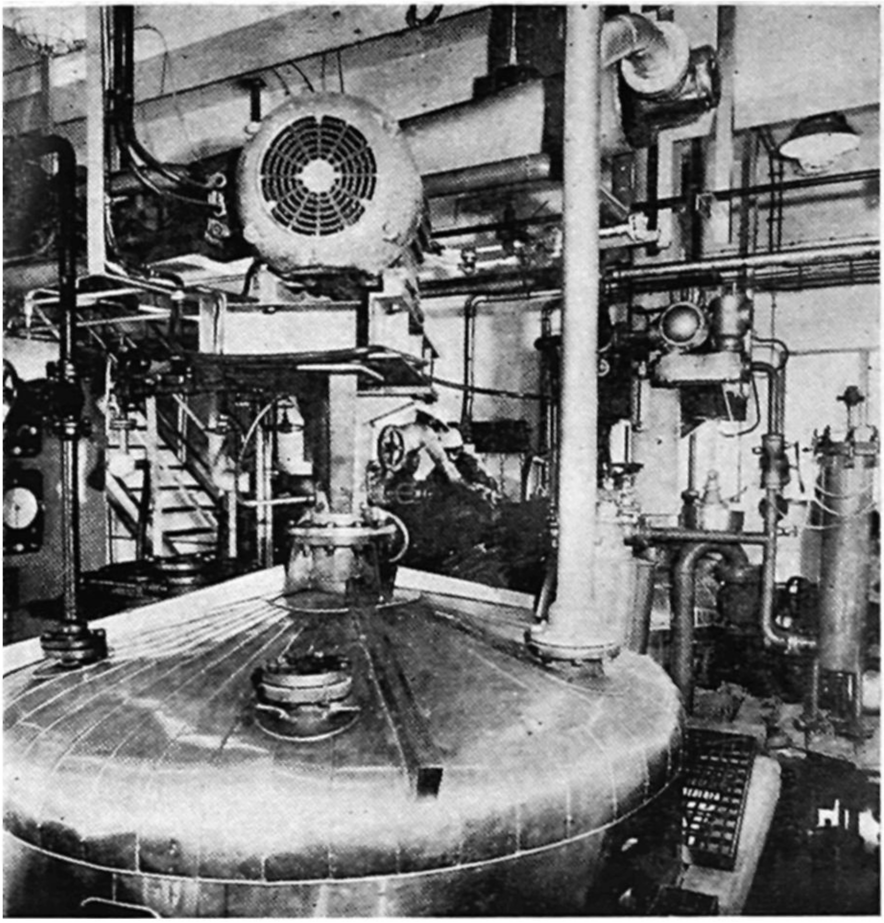


β-phenethyl alcohol plant - M/s Sunanda Aromatic Industries, Mysore.





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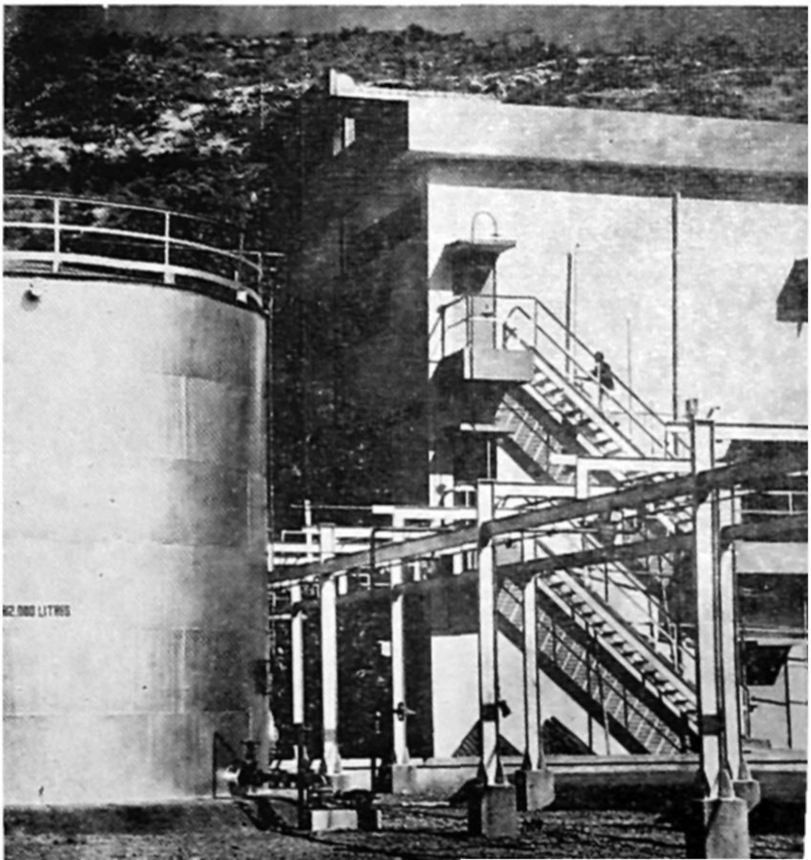
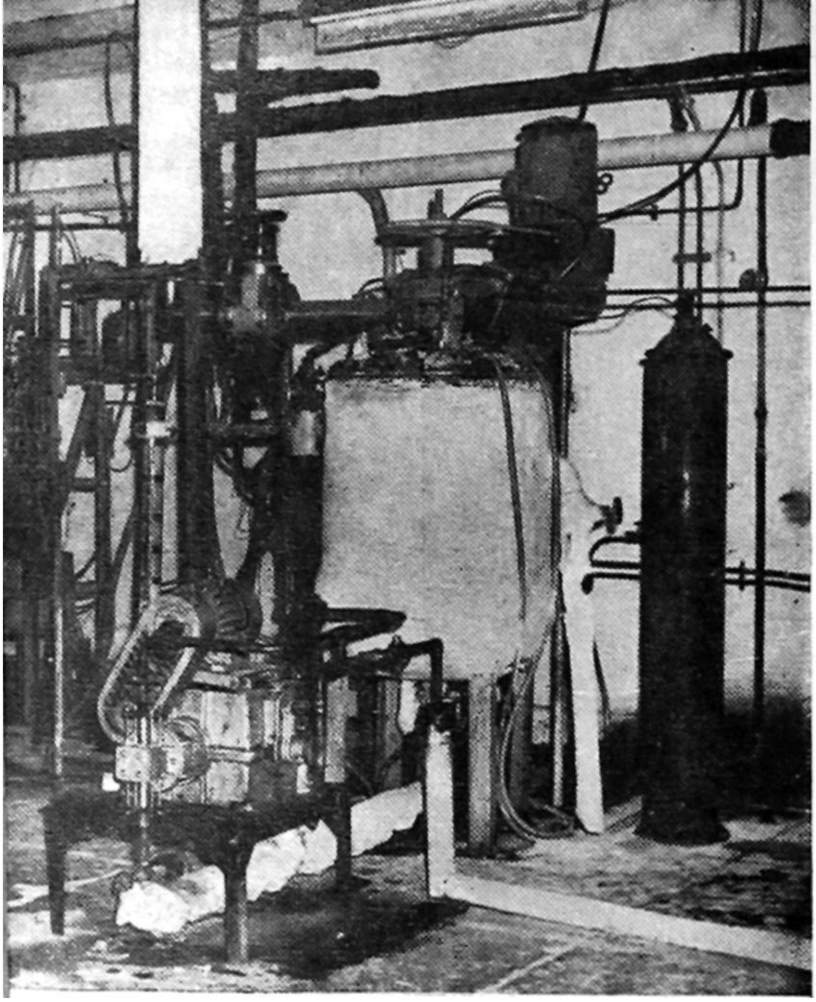
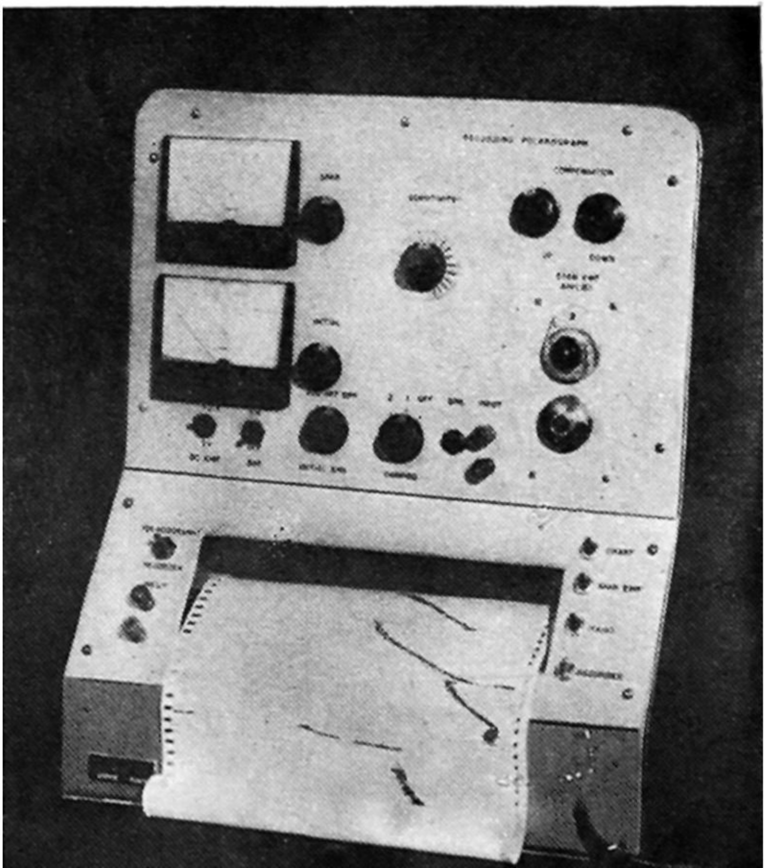




Ethylenediamine pilot plant at NCL



Proto- type D. C. Recording Polarograph

SPONSORED PROJECTS

PRIVATE PARTIES

INTERMEDIATES AND DYES

1. *Quinacridone pigments :* (SP-49/69)

Quinacridone pigments are characterized by high all-round fastness properties comparable to the phthalocyanines. The synthesis of translinear quinacridone was standardized. The sponsorship on this project ended on 30th November, 1970.

Since the termination of sponsorship, work has been continued to convert the crude quinacridone to a satisfactory pigmentary form and secondly to synthesise other substituted derivatives of quinacridone.

2. *Cationic dyes for acrylic fibres :* (SP-55/70)

Growing use of acrylic fibres in the country and their non-availability has created a need for undertaking developmental work on these dyes.

Preparation of a blue cationic dye has been standardized on a laboratory scale. Work has also been undertaken for the preparation of red and yellow cationic dyes.

3. *New Ingrain dyes :* (SP-59/70)

The project was sponsored with a view to prepare new Ingrain dyes. Ingrain dyes are in good demand because of their excellent fastness properties (e.g., Phthalogen Blue, C. I. Ingrain Blue 2). Technical preparation of an Ingrain dye desired by the sponsor was standardized and the project is now concluded.

TERPENOIDS AND PERFUMERY CHEMICALS

4. *Development of perfumery products based on longifolene and isolongifolene :* (SP-53/70)

In the Indian turpentine oil the pinenes are present to the extent of nearly 25% as against the pinene content of 90% in foreign turpentine oil. The present uses of the turpentine oil are therefore based on the chemistry of pinenes. Since the Indian turpentine oil contains large quantities of longifolene and Δ^3-carene, and some isolongifolene it is necessary to find suitable outlets for the commercial utilization of these components.

Earlier in the scheme, longifolene was converted into some derivatives having perfumery value and the details were supplied to the sponsor. However, during the preparation of these derivatives a part of the longifolene isomerises to isolongifolene.

Attempts are now being made to convert isolongifolene to a number of compounds of possible perfumery value. Out of a few such compounds two appear to be very promising. Experimental conditions for these selected compounds are being optimized on 1 kg./batch scale.

5. *Development of perfumery products based on Δ^3-carene :* (SP-54/70)

Four perfumery compounds so far derived from Δ^3-carene were accepted by the sponsor and their production has been initiated. With a view to characterize these compounds work on structure determination was undertaken. They were purified by using different techniques, such as column chromatography and preparative GLC. Structure determination of all these compounds is nearing completion.

A method for the preparation of the ketal from the acetylcarene has been standardized and the compound sent to the sponsor for its odour evaluation.

In addition to this work, Δ^3-carene was hydrogenated and the product purified by perparative GLC. This has been identified as carene by IR, NMR and MS techniques.

Oxidation of Δ^3-carene was attempted wherein one major and several minor products were obtained. Conditions are being standardized to get the major product in better yields.

6. *Coumarin :* (SP-51/69)

This perfumery chemical is not at present produced in the country and the imports are to the tune of 27 TPA valued at Rs. 7·5 lakhs.

A process for the manufacture of coumarin (perfumery grade, free from chlorine) was standardized on the laboratory scale. The details have been forwarded to the sponsor who intends carrying out pilot plant runs at their factory site. The project is now concluded

DRUG INTERMEDIATES AND PHARMACEUTICALS

7. *8-Hydroxyquinoline :* (SP-43/68)

This is an important intermediate required for the manufacture of anti-dysentry drugs. Even though a few parties have been licensed to manufacture this chemical, it is still not being produced in India and is entirely imported at present. During 1969-70, 31·5 T of 8-hydroxyquinoline and salts valued at Rs. 8·7 lakhs were imported.

After standardizing the process on 1 kg./batch scale, the know-how developed was demonstrated on a pilot plant scale (10 kg./batch) to the sponsor. The project is now concluded.

8. *Glyceryl- ∝-mono-para-amino-benzoate :* (SP-56/70)

This compound is used for the preparation of certain cosmetic products. Several experimental batches for the preparation of Glyceryl- ∝-mono-para-amino-benzoate have been carried out and a few samples of the final product from different batches have been sent to the sponsor for evaluation.

9. *p-Nitroacetophenone :* (SP-57/70)

p-Nitroacetophenone forms the starting material for the manufacture of chloramphenicol by one of the two main commercial processes currently in use for its manufacture. *p*-Nitroacetophenone is at present imported and its demand by 1973-74 is estimated at ca. 250 TPA, valued at Rs. 65 lakhs.

Starting from ethylbenzene, a two step process which involves nitration and oxidation, has been worked out on a laboratory scale and a satisfactory grade of the product meeting the required specifications obtained. Further work is in progress.

10. *p-Phenetidine :* (SP-66/70)

p-Phenetidine is an important intermediate for the manufacture of phenacetin, a pharmaceutical. *p*-Phenetidine is at present being produced by only one firm in the country for their captive use and it is not readily available in the market. A scheme on the preparation of this chemical has been undertaken on behalf of the sponsor. During the period under review, several alternative commercially feasible routes were studied.

INDUSTRIAL CHEMICALS

11. *Production of rutile titania from Indian ilmenite :* (SP-52/70)

Rutile titania pigment is currently not being produced in the country. Import figures of rutile titania for 1969-70 were 4,258 T valued at Rs. 16·5 millions. The project envisages pilot plant trials for the production of titanium tetrachloride at the sponsor's site and development of a technically feasible process for burning of titanium tetrachloride in the presence of oxygen at high temperature to produce rutile titania first in the laboratory unit and later in a semi-commercial unit to be installed at the sponsor's site.

A shaft furnace for carrying out larger batch operation of carbothermic reduction of ilmenite was designed and constructed at the sponsor's site. Experiments using different grades of reducing agents were carried out and their reactive efficiencies determined.

Energy balances and material flow balances for the following processes have been completed and supplied to the sponsor :

1. Beneficiation of ilmenite
2. Chlorination of the enriched ilmenite
3. Chlorination of the rutile ore

Drawings for the chlorination reactor, ferric chloride trap, condensation set up and disposal of the effluents have been completed and communicated to the sponsor.

Designs for the pilot plant for oxidation of anhydrous titanium tetrachloride and ancillary equipment have been finalized.

12. *Maleic anhydride by the oxidation of benzene :* (SP-46/69)

During 1968-70, about 800 T of maleic anhydride, valued at Rs. 30 lakhs, was imported. This chemical which is not produced indigenously is a key intermediate for a number of ester type resins.

Attempts were made to develop a technically feasible process for the vapour phase oxidation of benzene to maleic anhydride using indigenous catalysts. A detailed assessment of eight catalysts, comprising over 100 runs, was carried out on a pilot plant reactor.

The sponsored scheme has been discontinued from September 1970. Attempts to improve the conversion efficiency of benzene to maleic anhydride have been now undertaken as a NCL project.

13. *Ketene from acetone :* (SP-58/70)

Ketene is a versatile intermediate for the manufacture of a variety of industrial chemicals such as acetic anhydride, aceto-acetic ester, and other acetyl derivatives. These chemicals are imported at present. The requirement of ketene is estimated at 500 TPA. Ketene can be manufactured either from acetone or acetic acid. The sponsored work starting from acetone has an advantage of providing an industrial outlet for excess acetone.

The work has been undertaken essentially to collect data for the design, of a 200 TPA plant. Investigations were carried out in an experimental assembly consisting of a reactor with fluidized-bed heating, an acetone recovery system, and a ketene absorption unit. The operating conditions have been standardized to achieve 70% yield on the basis of acetone consumed. The sponsor intends to continue further work at the factory and to install a 10-15 kg. / hr. unit based on the designs supplied by the laboratory.

MISCELLANEOUS

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

During the period under review, 15 organic compounds isolated or synthesized in the NCL were sent for biological testing.

15. *Butylated hydroxyanisole (BHA)* : (SP-50/69)

This chemical is used in various fuel and lubricating oils as an anti-oxidant and is also used in oils and fats in the food industry.

A process has been standardized on 0·5 kg. scale for the manufacture of BHA, starting from hydroquinone. The product was equivalent in specifications to the imported food grade anti-oxidant. The scheme is now concluded.

16. *Removal of silica from black liquor* : (SP-60/70)

Bamboo which is employed for the manufacture of paper contains a high percentage of silica which leads to the following difficulties during the operation of the pulping plant :

(i) formation of scales in the evaporators, and

(ii) obstruction in the flow of smelt in the smelting furnace by the formation of beehive structures and precipitation of calcium silicate along with calcium carbonate during causticization process to the effect that the latter cannot be used again for the preparation of quick lime..

At the instance of a paper pulp unit, work on the removal of silica from 'black liquor' (and also form 'green liquor') was undertaken. A procedure was developed for the removal of 97-98% of silica from dilute black liquor containing 7-10 g. of SiO_2/ litre and 17% total solids. To reduce loss of the alkali and the organic matter, experiments were also conducted with a black liquor sample containing 4·79 g. of SiO_2/ litre and 43·06% total solids.

Optimum conditions for removing silica present in the green liquor sample (13-14 g. of SiO_2/litre) were worked out. It was found that 96-97% of silica could be thus removed.

Attempts are in progress to minimize the alkali and organic matter losses during the process of silica removal.

17. *Methyl vinyl ether-maleic anhydride copolymer :* (SP-61/70)

Methyl vinyl ether - maleic anhydride copolymer is used in the manufacture of explosive compositions. At present this chemical is being imported.

Methyl vinyl ether was prepared from vinyl chloride and methanol. It was copolymerized with maleic anhydride to get polymers of different viscosities ranging from 0·1 to about 0·9. All the prepared samples were supplied to the party for evaluation. The scheme was concluded at the instance of the sponsor.

18. *Development of testing methods for ceramic compositions :* (SP-65/70)

The chemist from the sponsor was trained in handling instruments such as X-ray diffraction set-up, quartz spectrograph, differential thermal analysis set-up, saturation magnetization set-up etc. He was also trained in interpreting the results.

The following known systems were studied on these instruments :

(i) $BaO — TiO_2$
(ii) $NiO — ZnO — Fe_2O_3$
(iii) $BaO — Fe_2O_3$

The results were used to understand the kinetics of the solid state reactions at different temperatures.

The programme has been concluded.

19. *Oxy-urea :* (SP-64/70)

This chemical is used as an anti-crease for textile finishing. The objective of this sponsored work is to develop a process for dimethylol ethylene urea for use in textile fabrics.

This is a two-stage process, ethylene urea is prepared in the first stage, which is then reacted with formaldehyde to give dimethylol ethylene urea.

The reaction conditions for the preparation of ethylene urea were standardized on 1 kg./batch scale whereby an yield of 95-97% based on chloroform soluble matter was obtained. A few runs of the second stage of the preparation have also been taken. Data for the commercial unit are being collected by further large scale experiments.

CENTRAL AND STATE GOVT. INSTITUTES AND INDUSTRIES

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

This is a coordinated scheme initiated by the Health Ministry, Govt. of India, to study the chemical, pharmacological and clinical aspects of some of the reputed Indian medicinal plants. Work in NCL relates to the study of chemistry of medicinal plants.

The selected medicinal plants are extracted and the isolated constituents are then sent to another unit for testing their pharmacological activity.

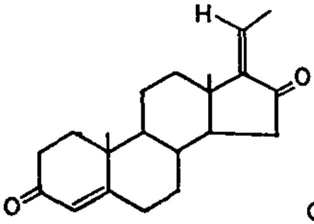
At present *Boerhavia diffusa Linn* (Punarnava), *Asparagus racemosus Willd* (Shatavari) and *Commiphora mukul* (Gugul) are being studied.

Boerhavia diffusa (Punarnava), *:* Pharmacological screening of the ethyl acetate sub-extract had shown anti-inflammatory activity. This sub-extract has now been divided into four fractions by chromatography on silica gel and these have been sent for pharmacological testing.

Authentic samples of this plant material have also been collected from different parts of the country. Their petroleum ether extracts have been prepared and sent for testing of diuretic activity.

Asparagus racemosus (Shatavari) *:* The major saponin present in the alcohol extract of Shatavari was found to have galactogogue property. It contains 5 to 6 monosaccharide units attached to the aglycone, sarsasapogenin. The same aglycone is also found to be present in one of the minor saponins. The monosaccharide units present in the saponin are two glucose units and one rhamnose unit. This minor saponin has also been sent for testing its physiological activity.

Commiphora mukul Hook ex Stocks : The gum oleo-resin of *Commiphora mukul* (Gugul) has been processed by a combination of solvent extraction, hydrolysis and extensive column chromatography over silica gel. The following known compounds were isolated and characterized : (a) Camphorene (b) Sesamin and (c) Cholesterol. In addition, Gugul also provides an easily accessible and good source for a number of useful steroids. At least four of them have been isolated in the pure crystalline form. Two of them, I (m.p. 192-193°) and II (m. p. 168-170°) are geometrical isomers belonging to the pregnane series and are being reported for the first time from a natural source (although both have been prepared synthetically, earlier). Compound I has been found to possess a high degree of anticholesterol activity. Compound III is a C_{27} steroid triol, (m. p. 225-228°). The assigned structures are fully supported by spectro-chemical data.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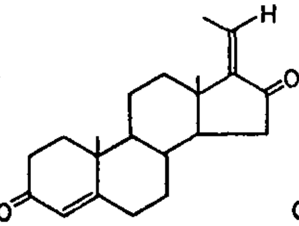
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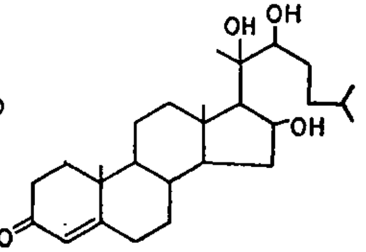
III

A continuous chromatographic column (89″x4″) was specially designed and fabricated for processing of large amounts (upto 500 g.) material at a time. Isolation of good amount (10 g.) of the biologically active steriod I (required for the activity tests) was rendered possible by use of this column.

21. *Constitution of lac :* (SP-24/61)

The scheme envisages investigations on the chemical constitution of lac resin. The structures of most of the lac acids and some other fractions of lac resin have been established so far. The knowledge of the structures of lac acids and the resin would be useful in modifying lac for newer uses.

The syntheses of jalaryl aleuritate and laccijalaryl aleuritate have been recently achieved. The above two esters, synthesized for the first time, are identical in all respects with the corresponding natural esters isolated from the soft resin of Palas (*Buteamonosperma*) seed lac. Condensation of the acid chloride of triformyl aleuritic acid and the δ-lactone of jalaric acid gave the product which on mild hydrolysis under specific conditions gave the required ester, jalaryl aleuritate. Laccijalaryl aleuritate was prepared from laccijalaric acid and the acid chloride of triformyl aleuritic acid.

Jalaric and laccijalaric acids on treatment with diazomethane gave the required esters in good yields.

22. *Extraction of morphine and other alkaloids from lanced poppy straw :* (SP-67/71)

Lanced poppy capsules which still contain some alkaloids are not put to any significant use. It is estimated that nearly 4725 T of lanced poppy capsules with a morphine content of 0·2% are available for extraction. The scheme has been undertaken (since Jan. 1971), with a view to develop a technically feasible method for the extraction of alkaloids from lanced poppy capsules.

Method for the estimation of morphine from poppy straw was modified. Powdered capsules were extracted with ammonical methanol in a soxhlet apparatus. The total alkaloids were then separated by passing through a cation exchange resin. Morphine which was separated from the other alkaloids by an anion exchange resin was estimated colorimetrically.

n-Butanol was tried as a solvent for the extraction of morphine from poppy capsules. Four successive extractions together gave about 71% of the total morphine present.

Attempts to separate codeine from thebaine quantitatively are in progress. This will help in standardizing a method for its estimation.

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

The work undertaken on behalf of Government of Jammu and Kashmir to determine the suitability of some of the Kashmir soft-woods for the manufacture of tyre cord grade dissolving pulp was continued.

In the earlier work, conditions for rayon grade pulp were established and some progress was achieved in the process for high purity tyre cord grade pulp.

The experimental work on tyre cord pulp is now complete. A process for the manufacture of super tyre cord pulp is developed. Samples of super tyre cord pulp were tested according to our processing conditions in the pilot plant of a tyre cord mill. The textile properties of tyre yarn produced are within the range of super I tyre cord yarn (Average O. D. tenacity g. p. d. 5·5, average O. D. cord strength lbs. 34·1).

24. *Acrylic acid/acrylates from acrylonitrile :* (SP-63/70)

Indian Petrochemical Corporation Limited, Baroda (IPCL), is planning to put up a plant for the production of 24,000 TPA of acrylonitrile. Although a major fraction of this production will be sold as such for the preparation of fibres and elastomers, a portion of the production is likely to be converted to acrylic acid and its esters which have a ready market in the polymer industry. The estimated requirement of acrylic acid and esters is 2000 - 3000 TPA. IPCL has therefore sponsored a project for developing the know-how for the technical preparation of acrylic acid and esters from acrylonitrile and to collect engineering data useful for designing of a commercial unit. The initial production of the acrylic acid and acrylates, may be worth around Rs. 2 crores annually and it is likely to go up to about Rs. 4 crores per annum in 4 to 5 years.

A process for the preparation of acrylic acid in over 90% yield based on acrylonitrile has been developed on a laboratory scale and further work is in progress.

25. *Propylene oxide :* (SP-62/70)

This is a major industrial chemical which is used in the manufacture of propylene glycol, polyester resins, polyglycol ethers, nonionic surfactants and alkanolamines. The proposed work envisages preparation of propylene oxide through the chlorohydrin route starting from propylene.

Work on this project has been recently initiated.

PL-480 SCHEMES

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

Basic investigations regarding thermodynamic properties of various refractory materials having potential importance in the ceramic industry were undertaken under this scheme. High temperature reactions of anhydrous metal halides (viz., halides of Al, Ni, Mn, etc.,) with the corresponding metals and also with metal oxides (viz., NiO, Mn_3O_4, MgO) were studied employing the transpiration technique.

The work on the scheme has been completed and final report has already been sent to the sponsor.

Work done during the year under report is given below :

(A) Studies on the equilibrium reaction between $CdCl_{2(c)}$ and $Cd_{(g)}$ by transpiration technique were carried out by passing cadmium metal vapour on solid cadmium chloride in the temperature range 675° - 775° K. The experimental results show the following stoichiometry for the reaction:

$$CdCl_{2(c)} + Cd_{(g)} = 2\ CdCl_{(g)}$$

From the experimental data the standard heat of formation [ΔHf_{298}] for $CdCl_{(g)}$ was found to be — 12 Kcal. / mole (the value reported in the literature being —9 Kcal./mole).

(B) *High temperature vacuum microbalance*

Vapour pressure measurement, by the Knudsen effusion method, has been made on a high purity (99·99% pure) sample of chromium metal in a platinum cell, the sample being contained in a tantalum cup inside the cell. An orifice area of $5{\cdot}539 \times 10^{-3}$ sq. cm. has been used for the purpose. The third-law value of $\Delta H^{298}_{sub} = 94{\cdot}55$ Kcal./ gfw agrees well with the second-law value of ΔH^{298}_{sub} = 92·25 Kcal./ gfw. These measurements within the temperature range of 1453° - 1673°K confirm the non-interaction between the sample and cell. This was further confirmed by metallographic examination of the used cell.

An intermetallic compound, Niobium dichromide, $NbCr_{2\cdot05}$ has been studied and similar type of platinum cells have been used as in the case of chromium. Vapour pressure calculations have been made on the basis of the pressure of monomeric species of chromium over the heated material. This has been made on the basis of a previous information obtained by mass spectrometric evidence. The results obtained are :

Tem. range °K.	Orifice area	"second-law" heat
1473-1703	$8\cdot935\times10^{-4}$ sq. cm,	106·00 Kcal./gfw (ΔH^{1609}_{sub} °K)
1522–1783	$2\cdot855\times10^{-3}$ sq. cm.	102·93 Kcal./gfw (ΔH^{1653}_{sub} °K)

27. *Wood phenolics :* (SP-28/66)

It was stated in an earlier report that the heartwood of *Morus laevigata* contains 3,5,4′-trihydroxydihydrostilbene. However, the non-identity of this compound with an authentic sample prepared by hydrogenation of resveratrol (3, 5, 4′-trihydroxystilbene) prompted a reinvestigation of the structure. A careful examination of the NMR and mass spectra suggested that this compound is 2, 4, 3′–trihydroxydihydrostilbene. Confirmation of this structure is being sought by synthesis.

The isolation of minor constitutents of *Morus alba* and *Morus rubra* is in progress.

Work on the heartwood and bark constituents of several *Artocarpus* species is being continued with special attention to the geographic location and age of *A. heterophyllus* and to the relationship of the polyphenolics in the bark, main trunk heartwood, and young branches of this tree. The conversion of artocarpin to cycloartocarpin has been attempted using *Aspergillus niger* (strain 612) and the product isolated appears to lack the CO group and one of the isoprene units.

The structure assigned to chaplashin, a novel seven-membered oxygen heterocycle isolated from *Artocarpus chaplasha* has been confirmed by a two-step conversion of dihydroartocarpin to dihydrochaplashin.

Since several flavonoids, with one or more isoprene units, have been isolated from various *Artocarpus* species, a systematic study of the mass spectral fragmentation patterns of these pigments has been made.

The bark of *Garcinia morella* had yielded morelloflavone, dihydromorelloflavone and two other compounds. One of these has been identified as morelloflavone, 7″-glucoside, isolated earlier by Japanese workers from *G. spicata,* and which has been also isolated from the bark of *G. cambogia* in this laboratory.

The isolation of two pigments (A) and (B) from the heartwood of *G. xanthochymus* has previously been reported. Preliminary results suggest that (A) may be an isomorelloflavone. Further work on (A) and (B) is under way.

Two new yellow pigments have been isolated from the heartwood of *G. pedunculata,* one of which is 2, 4, 6, 3′, 5′-pentahydroxybenzophenone (an isomer of maclurin). The structure of the other pigment is being investigated.

The isolation of minor constituents of *Taxus baccata* is being pursued. A fraction rich in the minor constituents has now been obtained by countercurrent distribution in a system comprising equal volumes of benzene, ethylacetate, methanol and water.

The effect of the following on teak tissue culture is being studied: (a) different sugars; (b) different inorganic nutrients as nitrogen source; and (c) different gibberellins.

Replacement of sucrose by fructose or maltose in Murashige's medium gave similar results, but increased growth was obtained with glucose and galactose. Since galactose has been found to inhibit other tissue and root cultures, its behaviour in teak tissue culture is being re-examined.

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PILOT PLANTS

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

Cellulose pulp as filler in plastics

In order to improve whiteness of plastic laminates, cotton linter pulp was treated with optical whiteners like Leucophore Rs, Bs and pulp samples were sent for testing at NuChem Plastics, Faridabad. The samples were found quite suitable as plastic filler.

Tyre cord pulp from Eucalyptus hybrid

Eucalyptus hybrid prehydrolysis sulphate pulp was processed at various temperatures and concentrations of sodium hydroxide with addition of a wetting agent. Conditions were established for getting pulp of 97% α — cellulose and pentosan content of 0·5 to 0·9%. A 7 kg. sample of tyre cord pulp from Eucalyptus hybrid was sent to a tyre cord mill for evaluation.

Eucalyptus hybrid, *Eucalyptus grandis* and Silver fir were treated by two-stage alkali pulping process. It is concluded that rayon grade pulp could be prepared from the above species by TSA process. Also there are indications that Silver fir pulp could be upgraded to tyre cord grade pulp.

Redrafting of the preliminary feasibility report on two-stage alkali pulping of bamboo and acid-prehydrolysis sulphate pulping of Eucalyptus hybrid has been completed. The final report has been circulated to project engineers, Govt. authorities and interested parties.

Silver fir tyre cord pulp prepared by NCL APS process was evaluated in a tyre cord mill in its pilot plant and found to give super cord of 34·1 lb. strength O. D. of tyre cord. This value falls well within the range of super tyre cord I.

2. *Bulk organic chemicals :* (PP-9/69)

The project particularly deals with the development of indigenous technology for the preparation of basic organic chemicals required in large quantities. During the period under report, developmental work on the preparation of terephthalic acid was conducted. Several follow-up actions to facilitate release of the already developed processes have been taken. The negotiations regarding the release of the processes for aniline, dimethylaniline, hexachloroethane etc., are in final stages.

Terephthalic acid (TPA)

This is the key intermediate for polyester fibre. Interest in TPA production specially centres around the fact that its use provides a single continuous process for polymerization and fibre spinning, thereby cutting capital cost by about 20% or more. The main problem in this route is to obtain high fibre grade purity TPA to eliminate the additional process of making a dimethyl compound of the diabasic acid for purification. At present a plant for dimethyl terephthalate (DMT) is being set-up at Koyali (Gujarat) and is expected to be in production in 1972-73. Based on imported know-how another plant is likely to be taken up in Assam. However, from the present developments it is clear that polyester fibre production in future will turn increasingly in favour of TPA. Since India will need more and more of polyester fibre, and since the fees and royalties for the foreign know-how are excessive, it is important to develop our own technology for TPA.

Terephthalic acid was prepared by isomerization of phthalic acid in accordance with Henkel process I. As a result of about 40 experimental bench scale runs, it was found that the process worked to satisfaction. The process was also tried with recovered raw material. The other aspects of the process, such as recovery of catalyst and potassium value were also investigated. The preparation of terephthalic acid by the phthalic anhydride route seems to be economically feasible. However since there is appreciable shortage of phthalic anhydride throughout the world and also that it has a very wide field of application in making of other chemicals, the preparation of terephthalic acid by this process was discontinued.

The preparation of terephthalic acid is now being tried by Henkel process II i.e., disproportionation of potassium benzoate. About 50 experimental bench scale runs have been taken.

Chlorination of methane

This process for producing carbon tetrachloride and chloroform by chlorination of methane gas is being jointly developed by NCL and M/s. Standard Mills Co. Ltd., Chemicals Division, Thana. After successfully operating the experimental unit consisting of 150 mm. dia. fluidized bed reactor (giving 2·5 kg./hr. product), a 300 TPA semi-commercial plant for carbon tetrachloride and chloroform has been designed and commissioned successfully by the firm with the assistance of NCL staff.

3. *Fine chemicals project :* (PP-7/64)

The Fine Chemicals unit has for the second consecutive year made a profit of Rs. 0·23 lakhs on total sales of Rs. 2·20 lakhs. As in the previous year, stress was laid on making the project economically viable.

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

Year	*Production*	*Sales*
1968-69	2·43	2·42
1969-70	2·35	2·71
1970-71	2·07	2·20

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

In this multipurpose project, scale up work on batch type processes which have already been developed on laboratory scale are undertaken.

There is a growing interest from the industry for developing the know-how for the manufacture of a variety of organic chemicals and intermediates which are produced by batch processes and are imported in substantial quantities. A tentative list of projects for which the know-how will be scaled up on pilot plant scale includes : dye intermediates, copper phthalocyanine pigments and dyes, rubber chemicals and plasticizers, textile auxiliaries and finishing agents, insecticides, fungicides and weedicides etc.

Processes for pilot plant work in this project are selected on the basis of imports and demand pattern in the country and the interest shown by industry for commercial exploitation.

p-Nitrophenol

The manufacture of *p*-nitrophenol on ca. 20 kg./batch scale has been carried out and the process has been standardized on pilot plant scale. Samples of the pilot plant batches have been analysed by various parties and have been found to conform to standard specifications.

Catechol and tert-Butylcatechol

The process of isolating catechol from polyvalent phenols (obtainable from Neyveli Lignite Corpn., Neyveli) developed on the laboratory scale was scaled up to 25 kg. catechol rich cut per batch and standardized.

A few more batches on the preparation of tert-butylcatechol from the catechol obtained above were also carried out on large scale.

These processes have been satisfactorily demonstrated to the party who has been licensed to exploit the know-how.

Monochloroacetic acid (MCA)

A series of runs for the preparation of monochloroacetic acid have been carried out with a modified set of reactors using a new catalyst. Methods have been developed for isolation of MCA from the reaction product. A process for making sodium salt to monochloroacetic acid has also been developed. The know-how on MCA and its sodium salt will be further developed on a commercial scale in cooperation with an industrial unit which has offered to buy this know-how.

1,1-Dimethylbiguanide hydrochloride

This is a useful hypoglycemic agent. Presently the consumption of this drug in India is about 700 kg. valued at about Rs. 90,000.

As a few industrial parties are interested in the manufacture of this anti-diabetic drug, its technical preparation was undertaken. After optimising the process on a laboratory scale, a few large scale batches were taken. A sample of the product was sent to an industrial concern for evaluation. The process is ready for exploitation.

2,2,4-trimethyl-6-ethoxyquinoline

This is an important antioxidant and flex-cracking inhibitor for rubber. A process for the preparation of this compound has been optimised on 1 kg. scale.

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PRODUCT ORIENTED RESEARCH

MATERIALS FOR SOLID STATE DEVICES

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

A successful demonstration of the NCL process for the preparation of cadmium sulphide photoconductive cells was given to another party which has recently started trial production.

After successful completion of the earlier part of this project, efforts were diverted to develop the photoconducting cells with higher power dissipation ratings by using new encapsulation techniques.

A crystal growing furnace with a new improved tube geometry was constructed; it features a 750 mm. quartz tube in place of the sintered alumina tube thereby eliminating wall porosity. A series of runs were taken and the crystals are in the process of evaluation.

A new encapsulating material based on polyester resins was successfully used for CdS crystals and large area photocells.

A technique for fabrication of experimental large area photocells was developed. It involves co-deposition of CdS and donor materials followed by sintering treatment. Such cells have light/dark ratios comparable with CdS crystal photocells.

2. *Tin oxide potentiometer :* (ATT-61/70)

The tin oxide potentiometer is a new development which is being actively investigated abroad. It has several advantages over the conventional potentiometers. The Bhabha Committee Report had predicted a demand of Rs. 1·60 crores worth of carbon potentiometers by 1975, and Rs. 1·40 crores worth of wirebound potentiometers, aggregating to Rs. 3 crores. The demand for tin oxide potentiometer will mainly depend on how far it will replace presently used carbon potentiometers. Its main application would be in radio and TV receivers, oscilloscopes, counters, military equipment, public address equipment, etc.

A new tin oxide power variable potentiometer with infinite resolution was fabricated in prototype form.

An experimental device less than an inch in diameter was successfully and conveniently operated at 4 watts. Further development is in progress.

Work on fabrication of furnace, deposition unit and standardization of test procedures and evaluation units was completed.

3. *Ferrites*

Ferrites are extensively used in electrical and electronic industries. The demand is growing rapidly and is expected to be around Rs. 1 crore per year for hard ferrites alone.

The NCL process on hard ferrites is released to two parties, one of the licencees has already gone into production.

3·1 *Oriented ferrites :* (ATT-10/59)

During the period, work on orientation process for anisotropic ferrite magnet has been completed. The laboratory runs have been successfully taken and magnets of energy product of 3·3 × 10^6 gauss × oersteds obtained. The composition, the orientation process and the heating cycle have been optimized. The samples have been examined by the licensee and found satisfactory. The demonstration and setting up of the orientation process is being carried out at their premises.

3·2 *Flexible magnets :* (ATT-170/71)

These magnets are used in refrigerator door gaskets. Several firms have shown interest in this product. Process development of these magnets is in progress on laboratory scale. Compositions containing a ferrite of 1μ particle size and PVC have been cast in small sheets and their properties studied. Efforts are being made to improve the physical properties of the flexible magnets to meet the requirements of the industry.

3·3 *Ferrites by co-precipitation techniques :* (AB-85/70)

An investigation is being made into the advantages of preparing ferrites and similar compositions by using active component oxides which should decrease considerably the temperatures of reaction and sintering. One of the techniques developed was to co-precipitate the concerned hydroxides with ammonia from a highly concentrated aqueous solution of nitrates. The water was evaporated and the ammonium nitrate decomposed *in situ.* The resulting material reacted and sintered below the conventional temperatures. This was confirmed by differential thermal analysis and by taking X-ray diffraction patterns of the material. One kg. of nickel manganite was prepared and sold to a firm on request.

3·4 *Pot-core compositions :* (AB-90/70)

The oxidising nature of nitrates does not permit the above method to be used as such for pot-core compositions where bivalent manganese is required. A suitable modification using oxalates has been worked out for producing pot-core ferrites. These ferrites need very specialized methods and techniques. These are being worked out employing highly active component oxides and avoiding oxidation of bivalent manganese. The results of the preliminary investigations are encouraging.

4. *Thick film materials :* (AB-75/69)

Thick film devices are gaining increasing importance in microelectronics industry particularly in the field of integrated hybrid circuitry.

The object of the work is to develop formulations of thick film materials, screen print on ceramic substrates, and measure the physical properties of the glazes.

Preparations of some thallium oxide and silver conductive pastes have been formulated.

Recently, M/s. Bharat Electronics Limited, Bangalore, have requested to undertake the preparation of certain silver conductive pastes which they are using for their ceramic capacitors. Three samples of imported pastes have been analysed chemically and their physical properties measured. Corresponding samples have also been developed. The submicron silver powder required for this paste has been prepared. It is further ball-milled in presence of certain protective chemicals. The paste is then prepared using predetermined portions of special glass frit, a polymeric binder, solvents and thinners.

5. *Polycrystalline silicon :* (ATT-9/69)

Silicon is used for making rectifiers, transistors, integrated circuits etc. Many firms have established production of several silicon devices from imported silicon. The present demand for polycrystalline silicon in the country is estimated at 500 kg./year worth Rs. 10 lakhs.

Preparation of high purity silicon has been undertaken by two methods :

(i) preparation of silane (SiH_4) and its thermal decomposition to Si;

(ii) preparation of trichlorosilane ($SiHCl_3$) and its hydrogen reduction to silicon.

Both the methods have some advantages and disadvantages. The silane process gives better yield and purity but it uses imported lithium aluminium hydride and the processing and handling of silane are hazardous. On the other hand, trichlorosilane process involves less foreign exchange component, but the product generally does not attain the same degree of purity as in the silane process.

A special room has been constructed providing clean and dust-free atmosphere. This is essential for any work on semiconductor, preparations and processing.

Silicon tetrachloride has been produced, as and when required, in a 5 kg./hr. preparative unit. Purification of $SiCl_4$ by subjecting it to chemical treatments, fraction distillation and adsorptive technique was carried out in all quartz units. The product was analysed mass-spectrometrically. No lines other than due to silicon compound were observed in the spectrum.

Secondly, a set-up made of high purity silica for the preparation of SiH_4 from $SiCl_4$ and $LiAlH_4$ was fabricated and installed. Several types of decomposition units for SIH_4 were tried. Work is in progress on standardizing the conditions for silane decomposition.

Both the $SiCl_4$ purification and silane preparation units are housed in a specially constructed Perspex cabin provided with gloves for operation from outside.

A unit to prepare $SiHCl_3$ has also been fabricated and several trial runs have already been taken. Hydrogen reduction of $SiHCl_3$ is being attempted.

6. *Magnetic properties of acicular gamma ferric oxide :* (AB-45/68)

Magnetic material used for coating recording tapes consists of gamma ferric oxide especially with an acicular crystal habit. The present requirements of the magnetic tape industry recently started in India is about 6·5 TPA and it is expected to rise up to about 30 TPA in about 5 years.

The particle size and shape of gamma ferric oxide prepared from hydrated ferric oxide precipitated by bubbling air through ferrous sulphate solution in the presence of scrap-iron, were studied with the help of an electron microscope. The product was found to be acicular in nature with particle size less than 1 micron and length to breadth ratio of 10:1 to 25:1. The magnetic properties of this material were studied by determining the coercivity and remanence, and these were found to be comparable with those of an imported sample.

A larger precipitating tank and a rotary furnace are being set up in order to scale up the process.

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

During the past few years substituted synthetic zeolites (molecular sieves) which are mainly crystalline sodium aluminium silicates have come in prominence as specific catalyst materials for various reactions such as alkylation, isomerization and cracking of petroleum fractions. Use of such catalyst in the country is not known and data on imports etc., is not available.

Investigations on the vapour phase alkylation of benzene using modified zeolite catalysts to obtain primarily ethyl benzene was undertaken. Towards this, a few catalysts based on x-type zeolites were prepared, and their catalytic activity is being tested. Preliminary study showed encouraging results. For the measurement of the adsorption of water, alcohol and benzene vapours on the catalyst samples under isothermal and isomeric conditions, an all glass gravimetric unit was fabricated and standardized. The measurements on the adsoprtion of water vapour on the catalysts samples at different vapour pressures and temperatures are in progress.

8. *Synthetic gem stones :* (AB-78/70)

Synthetic sapphire and ruby are used in the form of jewel bearings in scientific instruments, watches, meters, etc. These are also largely used in jewellery. The technique involves preparation of single crystals of alumina in an oxyhydrogen furnace. This flame fusion technique developed by A. Verneuil provides the best method for growing single crystals of high melting materials.

A laboratory model of the Verneuil furnace was set up. It consists of an inverted oxyhydrogen burner through which fine powder of alumina is dropped through the flame and collected on a refractory rod inside a refractory block. Modifications of this unit were tried to study the control of flame and feed rate. Trial runs for the growth of sapphire crystals were successful. Further studies are in progress to improve the efficiency and to incorporate automatic controls.

INDUSTRIAL INORGANIC CHEMICALS

9. *Iron oxide pigments :* (AB-79/70)

Synthetic iron oxides find extensive use as pigments on account of their relative cheapness and stability of their colours. These pigments are generally produced from ferrous sulphate which is a by-product in some industries. The direct calcination gives ferric oxide in various shades of red depending upon he temperature control. The preparation of hydrated ferric oxide pigments of various shades is under investigation.

Utilization of a by-product iron oxide sludge as pigment was studied. It was found possible to convert it to some shades of brown, chocolate and dull red. The particle size of these products, however, is not very fine, on account of which these can be used only as cheap filler pigments in linoleum, ceramics, etc.

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

The market for silicones and silicone formulations is expanding rapidly in the country, current annual requirement being of the order of 100 T valued conservatively at Rs. 40 lakhs. Since the requirement still falls short of an economic production of the chlorosilane intermediates, these are imported at present. There was a proposal also for importing the siloxane low polymer ('tetramer' mixture) as the intermediate instead of the more hazardous dichlorosilanes for polymerization to silicone oils in a single step.

A laboratory research programme on the methyl silicone intermediates, which form the bulk of the requirement for all silicones, was formulated in 1966. It consisted of (a) establishment of direct synthesis conditions to obtain a high single-pass conversion of methyl chloride into chlorosilanes with a high dimethyl dichlorosilane content in the chlorosilane mixture, and (b) isolation of the dimethyl siloxane intermediate from the mixture by an alternative route to fractional distillation of the chlorosilanes, that could be operated on a scale commensurate with the country's requirement. The laboratory results are summarized below:

Under the operating conditions (400 g. Si; liquid yield 1 kg. at 120 g./hr; MeCl conversion 80-85%), the laboratory reactor produces a liquid mixture principally of dimethyl dichlorosilane (above 60%, calculated on the pure dimethyl siloxane 'tetramer' isolated), and methyl trichlorosilane, trimethyl chlorosilane and methyl hydrogen dichlorosilane, probably in that order of abundance. By a process of esterification and fractionation with dry methanol, the methyl trichlorosilane was obtained as the tri-ester (in methanol), and both methyl dichlorosilane and dimethyl dichlorosilane were obtained as their siloxane low polymer fluids on hydrolysis of the distillates. The trimethyl component associates itself with the dimethyl fraction, with the result that the isolated dimethyl siloxane 'tetramer' consists principally of end-stopped linear dimethyl siloxane low polymers, which can be polymerized to the appropriate dimethyl silicone polymer in the usual way. The methanolic methyl trimethoxysilane is usable as such for surface treatment of structural materials (wood, masonry, plaster work) for water repellency.

The work in progress in this laboratory and two laboratories of the Ministry of Defence has been under periodic review by the Planning Commission. Based on the laboratory scale work, a pilot plant unit consisting of a preheater a mechanically stirred reactor and a condenser has been designed. These equipments have been fabricated and the pilot plant is ready for operation. The pilot plant envisaged in the NCL will handle about 20 kg. silicon per batch and produce 50 kg. of Rochow liquid at an average rate of 1 kg./hr. Each batch is expected to yield over 12 kg. of the fluid siloxane hydrolysate and a methanolic solution of methyl trimethoxysilane, thus making available sample quantities to industry for trial experiments in processing them to commercial products.

Development of some of the simpler commercial silicones and silocone formulations from the above intermediates are in view.

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

The commercial ethyl silicates are polymerized ethyl esters of silicic acid in which the silica content is varied during its preparation for making it suitable for different applications. The best known product ES-40 (silica content 40% by wt.) is mainly used for investment casting of high melting metal and alloys.

Authentic data on the imports and requirements of ES-40 are not available. Several letters were sent out to parties in the foundry and other similar fields. Industry has generally shown an encouraging response. It is therefore estimated that the demand of ES-40 may be of the order of 100 TPA in the near future.

Starting with silicon tetrachloride, the preparation of ethyl silicate-40 on a laboratory scale of 1 kg./batch was standardized. Half litre (500 ml.) samples were sent to a few parties for their evaluation. The samples were found suitable and the parties showed interest in purchasing large quantities of the product for their regular use. The sample was also sent to National Metallurgical Laboratory, Jamshedpur, which reported that the NCL sample was as good as the imported sample.

As an integrated project with the manufacture of ES-40, work on the preparation of the $SiCl_4$ at medium temperatures (about 400°) was undertaken. The investigation aimed at carrying out the chlorination of Indian ferrosilicon at a conveniently low temperature (to avoid problems of materials of construction) and also make the reactor thermally self-sustaining and continuous. Anhydrous hydrogen chloride gas, which comes as a by-product from the esterification reaction is used partly for the enrichment of ferrosilicon and partly for the preparation of trichlorosilane ($SiHCl_3$) which is a well known material for the manufacture of transistor grade silicon.

12. *Aluminium silicate :* (ATT-121/69)

Aluminium silicate having about 70% silica content, low bulk density high purity and uniform particle size is used as a filler in rubber and plastic industry. It finds use in rubber soleing materials of all types, since it toughens the raw mix, minimises the need for accelerators and gives the vulcanizate a superior hardness and other desirable properties. The requirement of this material is mostly met through imports. The imported product costs about Rs. 3,000/- per T. A firm in Poona alone uses about 36 TPA.

Aluminium silicate was prepared from freshly precipitated silicic acid and alumina on 400 g. scale. M/s. Swastik Rubber Products, Poona, reported that these compare well with the imported ones. Samples have also been sent to M/s. Indian Rubber Manufacturers' Research Association, Thana, for testing and evaluation.

Attempts are being made to prepare aluminium silicate similar to the imported variety [silica 69-70%, alumina 7%, alkali (Na_2O) 6-7% and loss on ignition 15-16%] in composition and properties.

Further developmental work will be undertaken if the work on the project is sponsored by the industry.

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

The work was initiated at the instance of the Indian Veterinary Research Institute, Mukteshwar, who have reported that the demand of 'Alhydrogel' is of the order of 100 TPA valued at Rs. 10 lakhs. Further it is reported that the entire demand of the country is met through imports.

Few samples of aluminium hydroxide gel have been prepared from commercial aluminium sulphate and ammonia. In composition and physical properties, these samples compare well with the imported 'Alhydrogel'. However, field trials on the product have yet to be carried out.

14. *Utilisation of mineral Wollastonite :* (ATT-80/70)

Wollastonite, a naturally occurring calcium metasilicate is useful in insulation, ceramics, rubber, paper, plastics and paint industries due to its fibrous crystal structure. At present it is mainly used in ceramics. In order to find other industrial outlets for the deposits of Wollastonite in the country, attempts have been made to prepare hydrated calcium, magnesium and aluminium silicates.

Preliminary experiments on the preparation of calcium, magnesium and aluminium silicates from Wollastonite mineral have shown encouraging results.

A party engaged in mining of Wollastonite has recently (June 1971) sponsored work on the production of calcium silicate from Wollastonite. Their annual requirement of hydrated calcium silicate is about 3000 to 4000 T valued at Rs. 35 lakhs.

15. *Cadmium pigments :* (AB-81/70)

Cadmium sulphoselenide pigments worth Rs. 39 lakhs per annum are imported, to meet the indigenous requirement of the industry. These pigments find extensive use in plastic, ceramic and printing industries because of their fastness and resistance to heat and alkali.

Technical preparation of yellow, orange and red shades has been undertaken.

The oil absorption values of the pigments were determined and found to be comparable with the imported pigments except for the yellow pigment. The particle size of the pigments prepared is in the range of 0·9 to 1·1 μ, as determined by optical microscopy. Experiments designed to yield smaller particle size, approaching that of the imported quality (0·5 to 0·9μ) are in progress.

16. *Superphosphate from indigenous rock phosphates :* (ATT-144/69

Due to inadequacy of proven rock phosphate deposits of suitable quality in the country, most of the requirements of phosphate rock are met through imports. Deposits available in the country such as Maton rock phosphate and Jhamal Kotra rock phosphate are either of low phosphate content or insufficiently reactive.

Increased solubilisation of Maton rock phosphate by addition of 5% by weight of ammonium nitrate was reported earlier. However, this method did not improve to any appreciable extent the reactivity of Jhamal Kotra rock phosphate which at the moment is the single largest source (about 100 million T) in the country. Even so, since the P_2O_5 content of this phosphorite exceeds 34%, the water soluble P_2O_5 in the superphosphate prepared from it is over 17% to admit its use without further treatment. Calcination of the Jhamal Kotra rock phosphate alone and with additives like sodium chloride and carbon also did not enhance its reactivity above 86 to 88%.

17. *Vitamin B_6 (Pyridoxine hydrochloride)* : (ATT-16/66)

During past few years there has been considerable development abroad in the processes for synthesis of Vitamin B_6 which is an important drug. As a result there has been a steep fall in the prices of this drug. The U. S. prices of Vitamin B_6 which were around \$515/kg. in 1950, stood at \$80/kg. in 1960, and at \$23/kg. (Rs. 173/kg.) in 1970. The average c.i.f. price of the imports for the year 1969-70 works out at around Rs. 153/kg. However consignments from various countries indicate c.i.f. prices between Rs. 120 to Rs. 175/kg. Vitamin B_6 is not manufactured in the country and its imports amount to nearly Rs. 13 lakhs per annum.

The earlier process starting from *dl*-alanine consisted of a five step synthesis. Critical cost evaluation of the process showed that although the yields were high the foreign exchange component and the cost of the final product were prohibitive for its commercial utilization in the country.

It was, therefore, decided to critically review the new methods of synthesis and work on a commercially feasible process was initiated. Starting from paraldehyde, a four step synthesis has now been developed on laboratory scale in which 4-methyl-5-ethoxyoxazole is the key intermediate.

The process is being offered for its commercial utilization through NRDC. It is proposed to undertake larger trials of the process for demonstration to interested parties.

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

A systematic study of various indigenous sources for colchicine which is used in pharmaceuticals and also plant breeding, revealed that a new plant source can yield this alkaloid in higher yields than *Gloriosa superba*. (Hindi-Harihari). Large scale cultivation of this plant has been arranged with the Botanical Survey of India, Poona, A patent (Application No. 127743) on "A process for obtaining colchicine from a new plant source", has also been filed.

With a view to study the effect of variations in soil and climate conditions on the colchicine content, the isolation and estimation of colchicine in different seed samples supplied by the Botanical Survey of India, Poona, has been carried out.

19. *Camphene to camphor* : (ATT-148/69)

Camphor is an important industrial chemical used as a plasticizer for cellulose nitrate in the manufacture of photographic films and as an odorant/flavorant in pharmaceutical and household products. Camphor is indigenously produced by one firm and has not been imported for the last 3 years.

Work has been undertaken to simplify the currently used three-step route for preparing camphor from camphene, which in turn is obtained by isomerization of α-pinene. After considerable trials it has been possible to effectively reduce the amount of dichromate used in the oxidation without impairing the yield (80-82%) and purity of camphor. After optimization on a small batch (100 g), the process has been scaled up to a charge of 500 g. of camphene.

However, on economic considerations a 10% increase on the 80% yield of camphor, so far obtained, appeared desirable. Further work on standardization of reaction conditions, aimed at minimizing the loss of camphene by drastic oxidation to carbon dioxide in a side reaction, has therefore been undertaken.

20. *Quinine to quinidine* : (AB-82/70)

Quinine is the major alkaloid present in the cinchona bark. Quinidine is one of the minor alkaloids present in the same plant. However, quinidine fetches a higher price than quinine. In 1968-69 quinine and its derivatives worth about Rs. 93 lakhs were exported.

Preliminary experiments have shown that quinine can be converted to quinidine economically. The yield of quinidine is about 40 %, and about 40% of quinine is recovered. Experiments up to 100 g. scale have been conducted. Some difficulties faced on larger runs are being overcome and the procedure is being standardized.

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

Theophylline and caffeine are widely used in pharmaceuticals. Theophylline is a myocardial stimulant and diuretic whereas aminophylline, a derivative of theophylline, is useful in bronchial asthma.

Theophylline and aminophylline are not manufactured in India. Only caffeine is being manufactured from tea waste by a few firms. During 1969-70 the imports of theophylline, aminophylline, caffeine and its salts were 41·4 T valued at Rs. 12·7 lakhs.

Starting from 1,3-dimethylurea, a convenient method was developed for the synthesis of theophylline IP (1 kg./batch) during 1969-70. Processes for the preparation of caffeine IP (0·5 kg./batch) and aminophylline (0·5 kg./batch) starting from crude theophylline have also been standardized.

The processes are being offered to industry.

22. *Vitamin D_3 :* (ATT-140/69)

Vitamin D_3 has anti-rachitic activity and is used in the pharmaceutical and food industries. During the period April-September 1970, Vitamin D (D_2 and D_3) valued at Rs. 1·91 lakhs was imported. Vitamin D is also manufactured in the country possibly from the imported penultimate intermediates. It is however estimated that the demand in the country for Vitamin D_2 and D_3 may be worth Rs. 10 lakhs per annum.

7-Dehydrocholesteryl benzoate has been prepared in satisfactory yields by carrying out the allylic bromination of cholesteryl benzoate and dehydrobrominating the resulting bromo compound. 7-Dehydrocholesterol (10 g./batch) has been converted to a crystalline derivative of Vitamin D_3. Work is in progress for scaling up all the steps.

23. *Sulphadiazine :* (ATT-81/68)

Sulphadiazine although indigenously made in the country is also presently imported to the tune of 163 TPA valued at Rs. 71 lakhs. The Indian manufacturers depend on the use of a costly key intermediate, 2-aminopyrimidine which is imported.

A simple process for the preparation of the 3-carbon intermediate 1,3,3-trimethoxypropene from a readily available material has been standardized. Thus in the route adopted for sulphadiazine, the use of 2-aminopyrimidine as an intermediate has been avoided.

Preparation of acetyl sulphadiazine from acetyl sulphaguanidine and sulphadiazine from sulphaguanidine by condensation with trimethoxypropene have been carried out under variety of conditions on a laboratory scale. It has been found that acetylsulphaguanidine gives acetylsulphadiazine of satisfactory purity in 80-85% yield. With sulphaguanidine, however, the yields of pure sulphadiazine obtained were only ca. 65% of theory.

Further developmental work on this project would be undertaken if specific interest is shown by industry.

24. *Propoxyphene :* (ATT-165/71)

Propoxyphene (α-*dl*-4-dimethylamino 3-methyl-1,2-di-phenyl-2- propionoxybutane hydrochloride; Darvon (R) is a good analgesic which finds extensive use in USA.

Preliminary laboratory work on the preparation of this new drug has been undertaken. Although the process consisted of several steps, the yields at the various stages were encouraging. Further developmental work will be undertaken on a sponsored basis.

25.. *Glyceryl guaiacolate :* (ATT-156/70)

Glyceryl guaiacolate is a pharmaceutical mainly used as an expectorant in cough remedies and in certain cases as intestinal antiseptic. Its import in 1969-70 amounted to 2 TPA (c.i.f. value Rs. 1·5 lakhs). This chemical is not yet manufactured in India.

A process for the preparation of guaiacol from *o*-anisidine was standardized earlier. A process for the technical preparation of glyceryl guaiacolate from guaiacol has been standardized.

PERFUMERY AND ESSENTIAL OIL PRODUCTS

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

Terpineol is used extensively as a perfumery chemical. Currently, a large part of our requirements of terpineol and its esters are being imported (Rs. 12·05 lakhs in 1969-70).

Perfumery grade terpineol is prepared in two steps. The first step *viz.*, the preparation of terpin hydrate, from α-pinene, was standardized earlier. The second step is the dehydration of terpin hydrate to terpineol. Different catalysts were tried for this step, and the effects of variation in pH and other parameters studied. A new apparatus was designed and fabricated so as to minimize the side reactions leading to off odours. The second step has been also scaled up to give 1 kg. of terpineol (over 99% purity) in a single batch.

The overall yields of terpineol, based on α-pinene, are nearly 79%.

The process has been referred to NRDC for releasing it to industry and negotiations with a few parties are in progress.

27. *Utilization of β-himachalene :* (AB-17/67)

The work has been undertaken for preparing industrially useful products by utilizing β-himachalene, a major constituent of commercially available *Cedrus deodara* Loud (Hindi-Deodar) oil.

β-Himachalene oxide obtained from β-himachalene has been tested for its juvenile hormonal activity against red cotton bugs. The preliminary report is encouraging.

The study on the insect hormonal activity of the oxygenated components of the essential oil of *Cedrus deodara* Loud, has also given encouraging results.

The preparation of dihydrohimachalene from β-himachalene has been standardized. Dihydrohimachalene has been oxidised and the products obtained are being studied.

28. *Autoxidation of ∝-pinene for the preparation of verbenone :* (AB-86/70)

Verbenone is an interesting compound for perfumery purposes. It is present in very small amount in Spanish verbena oil. Many unsuccessful attempts have been made in the past to synthesize it economically.

A number of experiments on the oxidation of ∝-pinene at different temperatures and experimental conditions have been carried out. These experiments have shown encouraging results. The analysis of the oxidized products by gas-liquid chromatography shows that verbenone and verbenol are formed in satisfactory yields. Further work on the oxidation step and separation of verbenone and verbenol is in progress.

ORGANIC INTERMEDIATES, DYES AND PIGMENTS

29. *Carbazole dioxazine violet :* (ATT-139/69)

These pigments are known to give bright violet shades which possess excellent fastness properties comparable to the phthalocyanines. Such type of pigments are not manufactured in India.

A four step synthesis of carbazole dioxazine violet pigment base has been standardized on 1 kg./batch product scale starting from technical grade carbazole of 95-97% purity.

Work on the conversion of this base to pigment Violet RL is in progress. A pigmentary form has been obtained that compares well with PV fast Violet BL when seen in bulk but gives slightly duller shades on testing. Attempts to improve the product are in progress.

30. *Utilization of methyl benzoate :* (ATT-142/69)

The Indian Petroleum Corporation Ltd., Baroda (IPCL), are installing a plant for production of dimethyl terephthalate as a part of the Gujarat Aromatics Project. This plant will yield nearly 300 TPA of crude methyl benzoate as a by-product. The project has been undertaken to explore the possibility of converting the above methyl benzoate into industrially useful products.

The major impurities in crude methyl benzoate to be obtained as a by-product by the IPCL have been identified by VPC and NMR spectra.

Larger quantities of this by-product were received in September 1970 and work was started on its conversion to benzoic acid IP. A process has been standardized on 1 kg./batch to give benzoic acid of IP specification. Batches on larger scale will shortly be undertaken.

31. *New synthetic dyes and pigments :* (ATT-157/70)

A series of dyes for synthetic fibres were prepared earlier in this Laboratory and covered by Indian Patent 116453. Encouraged by the earlier results a number of new azo disperse dyes containing various substituents were prepared. The effect of the substituents on substantivity and light and sublimation fastness properties, particularly on polyester fibres, will be studied.

A series of new dyestuff intermediates based on phenolic derivatives and containing groups which could modify the tinctorial and fastness properties were prepared. Pigments, disperse dyes and cationic dyes are being prepared by using these intermediates. They will be evaluated for their fastness properties.

A few pigments based on pyrrocoline chromophoric system were prepared. These are of interest because of their brilliance, tinctorial and fastness properties. A few pyrrocoline disperse dyes have also been prepared. Testing of these disperse dyes along with the other disperse dyes mentioned earlier will be undertaken.

Attempts were made to synthesize 1-carbethoxy-3,4-phthaloyl-2-thiaquinazoline by various routes. The reaction between 3-carbethoxymethylmercapto-2-chloro-1,4-naphthoquinone and pyridine was studied. In most cases, the corresponding pyrrocoline was obtained instead of the expected thiaquinazoline.

32. *Thioglycollic acid (Mercaptoacetic acid) :* (ATT-164/71)

This is a valuable chemical with several applications. It is used in hair fixative preparations. It is also an essential catalyst for the preparation of Bisphenol-A.

An attractive method for the preparation of thioglycollic acid from monochloroacetic acid has been optimized.

33. *Chlorinated copper phthalocyanine :* (ATT-155/70)

This bright green pigment with excellent tinctorial and fastness properties finds wide use in paints, plastics and printing inks. Large quantities of this pigment are imported in the country.

Two processes for the technical preparation of chlorinated copper phthalocyanine were standardized on a laboratory scale.

Efforts are now being made to improve the pigmentary characteristics of the product.

34. *Mucochloric acid :* (ATT-166/70)

Mucochloric acid is an intermediate used in some of the photographic preparations. It is reported to be imported to the tune of about 100 kg. valued at Rs. 2-3 lakhs per annum.

A laboratory process for the technical preparation of the chemical is being developed.

35. *Morpholine :* (ATT-159/70)

This versatile chemical is primarily used as an intermediate for rubber chemicals, and as corrosion inhibitor. Morpholine derivatives are particularly useful in the textile industry as softening agents and optical brighteners. The present imports of morpholine and its derivatives are in the range of 30-40 TPA, valued at Rs. 7 lakhs; the total requirement is estimated around 800 TPA.

Process development study on the preparation of morpholine by the dehydration of diethanolamine was undertaken. Several batch runs have been carried out in an all-glass assembly, and yields of over 80% are obtained. The procedure involving extraction with the organic solvent followed by distillation has been worked out for obtaining pure morpholine. The work on this project has been concluded, and the process is being offered to industry.

36. *Ethanolamines :* (ATT-160/70)

Ethanolamines have assumed great importance in recent years because of their various uses in detergents, gas scrubbing, textile chemicals, cosmetics and toilet products. During the period 1969-70, about 1700 T of mono, di, and triethanolamines were imported at a cost of about Rs. 42 lakhs. The indigenous demand is estimated at more than 3000 TPA. Raw materials for the production of ethanolamines; namely, ammonia and ethylene oxide, are indigenously available. The project work was undertaken with the objective to develop a batch process for ethanolamines.

The literature survey, preliminary cost estimates, and experiments in a one-litre autoclave have been concluded. A few large scale experiments in a 14-litre reactor, with flexibility in operation in order to obtain higher percentage of mono and triethanolamines respectively, have been carried out. The results are under scrutiny, and attempts are being made to improve the yields.

37. *Ethylenediamine :* (ATT-58/68)

During 1969-70, 191 T of ethylenediamine, valued at Rs. 9 lakhs, was imported. The estimated demand for this important chemical used in fungicides, pesticides etc., is however around 1200 TPA.

A pilot plant of 5 kg./hr. was operated successfully for a period of 200 hrs. at pressures in the range of 100-250 psig., and difficulties faced during the earlier work were removed. Alongwith these continuous runs, 15 more batch-runs were carried out in a 10 litre autoclave to ascertain the reaction conditions. Studies on the analysis of reaction products were carried out by VPC and mass spectrometer. Separation techniques for obtaining pure amines were developed, and the continuous pilot plant was modified for operating at higher pressure with the objective to achieve total conversion of the raw materials to ethylenediamine and polylethylenepolyamines.

Based on the results, cost estimates and process design reports are prepared. The process will be ready for release shortly.

38. *Plasticizers :* (ATT-135/69)

There is a shortage of dioctyl phthalate (DOP) due to the shortage of 2-ethylhexanol. Since butyloctyl phthalate (BOP) can replace DOP in some PVC formulations, work on developing the process for BOP was undertaken. It is estimated that around 3000 TPA of BOP is likely to be used as a partial replacement for DOP.

The process conditions for BOP were standardized on the bench scale, as well as on the pilot plant. The samples compared very favourably with the imported sample. Six pilot plant runs of 45 kg./batch scale were taken to finalize the process conditions. The process has been offered to industry.

POLYSACCHARIDES AND RELATED PRODUCTS

39. *Surface acetylation of cellulose :* (ATT-158/68)

In this joint development programme to be carried out by NCL and Bombay Textile Research Association Bombay (BTRA), surface acetylation of cotton fabric is being attempted to improve its properties (especially its resistance to mildew and photochemical degradation). The work is in progress.

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

Hydroxyethyl starch (HES) is widely used abroad in textile sizing and printing. It possesses several advantages over conventional material like starch which is used at present.

The test report of HES samples indicated that these were inferior to the normal starch being used in textile printing. Use of HES in paper industries for tub-sizing and calendering has been advocated. Paper industries have been contacted for testing the HES samples.

41. *Cashewnut shell gum :* (AB-76/69)

Cashewnut shells are available in India as a waste in different factories and are used as fuel. A water soluble polysaccharide (CNS-gum) has been solated from CN shells in a yield of 8-9%. The polysaccharide is under investigation to explore the possibilities of its industrial use.

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

Large quantities of cellulosic wastes do not find economic use. Attempts are being made to obtain commercially useful products such as D-glucose from cellulosic waste materials such as, groundnut shells, sawdust, etc.

Work carried out earlier using gaseous hydrogen chloride and conc. hydrochloric acid for saccharification of cellulose gave 80% yield of D-glucose and a residual hydrocellulose was obtained as a black powder which could not be utilized. However, using dilute sulphuric acid and high temperature, conditions have been standarized to hydrolyse cotton and groundnut shell pulp to D-glucose to give a yield of nearly 92%.

43. *Rare sugars :* (AB-87/70)

Work is in progress on the preparation of the following rare sugars which are required in biochemical research. The present demand of these sugars in United States appears to be a few thousand kilos per annum.

Attempts are also under way to assess the present and projected demanp of these sugars in Indian and foreign markets.

2-Amino-D-glucose-hydrochloride

A waste from food canning industry has been found to be a good source of 2-amino-D-glucose-hydrochloride. Experiments are in progress to standardize the conditions for preparing this sugar.

L-Arabinose

Preliminary experiments have been undertaken to prepare this sugar from indigenous raw materials. Further work is in progress to standardize the conditions to obtain maximum yield of the sugar from the above source.

D-Galactose

A cheap natural indigenous source which contains 75% of D-galactose has been located. A few experiments have been conducted to prepare D-galactose from this raw material.

44. *Modification of starch :* (ATT-54/64)

Based on tapioca starch several products such as starch phosphate mono ester, starch phosphate diester, starch borate and carboxy methyl starch have been prepared on laboratory scale.

These modified starches find many applications such as thickner in food, bakery, confectionary, ice cream, in textile sizing, dyeing, finishing and as flocculant in ore refining etc. Samples of these starches are being sent to industry for their evaluation. Further developmental work on these derivatives will be undertaken after the samples are approved and users for the technology are identified. Efforts are also being made to get this work sponsored by industry.

45. *Modification of Guar gum :* (ATT-107/70)

Technical preparations of Guar gum acetate and carboxy methyl Guar gum have been undertaken with a view to assess their suitability as gum Arabic substitutes. Consumer acceptability of these products is being confirmed. On approval of the samples, further developmental work will be undertaken.

46. *Utilization of tamarind kernel powder :* (ATT-137/69)

Several derivatives of tamarind kernel powder (TKP) have been prepared on a laboratory scale. They are TKP phosphate, TKP phosphate diester, TKP borate, carboxymethyl TKP and other modified forms suitable for jute sizing and sizing in laundry. These products are under evaluation by industry.

47. *Sorbitol-Mannitol from invert sugar :* (ATT-55/66)

In view of the high prices of glucose in the country, the work on developing a process for sorbitol and mannitol by hydrogenation of inverted sugar was undertaken. Sorbitol is used as a humectant for tobacco and is also used in foods and the pharmaceutical industry; as starting material for Vitamin C and for a variety of surface active preparations. Mannitol also finds uses in medicine, resins and fermentation industry.

A laboratory process for the inversion of sugar and its subsequent hydrogenation was scaled up by taking several 25 kg./batch runs for the inversion step and 4 kg./batch for the hydrogenation step. 80% of the mannitol formed was separated as a somewhat impure product.

Use of deionized molasses solution in place of sugar was tried in a few experiments. However, due to the long period required for hydrogenation and the dark colour of the product, which could not be improved by active carbon treatment, molasses are found as an unsuitable substitute for sugar.

The project is now concluded, and the process is ready for release.

MISCELLANEOUS ORGANIC PRODUCTS

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

This is one of the most effective mosquito repellents known and is not being manufactured in India at present. Information about its imports or requirements etc., is not available.

The compound N, N-diethyl-*m*-toluamide is prepared by the oxidation of xylene to toluic acid which is then converted to toluamide. The oxidation of xylene has been scaled upto 2 kg./batch. Simultaneously, the problems of reuse of catalyst and recycling of recovered xylene have also been overcome.

A suitable reactor for the conversion of toluic acid to toluamide was designed and fabricated. A few trial runs have been taken. Attempts are now being made to scale up the condensation step. Meanwhile, field trials conducted by Defence Department on the NCL product have given satisfactory results.

49. *Saponin for photofilms :* (AB-88/70)

A saponin as an emulsifier is required by M/s Hindustan Photofilms, Ootacamund, to the tune of about 1500 kg./year.

By a simple procedure saponins were isolated from soapnuts and purified. The material was sent for testing and evaluation. The samples were found generally good but M/s Hindustan Photofilms have pointed out certain deficiencies to be remedied. Fresh samples are under preparation which will be sent for testing. After the approval of the sample the procedure will be standardized on a large scale.

50. *Shark repellent compositions :* (ATT-148/70)

At the suggestion of Defence, analysis of the imported shark repellent material was carried out, and a suitable indigenous substitute for the imported shark repellent composition was prepared in collaboration with a local dyestuff firm and samples sent to Defence authorities. The work on the project is now concluded.

51. *'Sonobouy' fluorescent dye marker :* (ATT-147/70)

This is also a Defence requirement; and the composition is presently imported. The imported sample was analysed and on the basis of its analysis, a suitable indigenous substitute was developed. A 10 kg. sample has been sent to Naval Physical and Oceanographic Laboratory, Cochin, and their report is awaited.

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

Good quality low temperature organic fluxes used for soldering electrical contacts and coating welding rods are not manufactured in India, as some of the raw materials are not available.

A composition has been made which has been approved by industry and a sample sent to a party interested in its commercial utilization for consumer acceptability trials.

53. *Flocculants for coal slurry :* (ATT-167/70)

This work has been undertaken in collaboration with CFRI, Dhanbad. These compounds are required to be used as sedimentation aids in coal washeries for clarification of washery water.

Ten samples have been sent for testing and further work will be undertaken on the basis of their test report.

INDUSTRIAL POLYMERS AND RELATED PRODUCTS

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

Nitrile rubber, a copolymer of acrylonitrile and butadiene, is primarily valued for its oil resistant properties. It is also used in special adhesive formulations. Nitrile rubbers are not manufactured indigenously so far. Their estimated annual requirement is around 800 T valued at Rs. 80 lakhs. Among the different grades of nitrile rubbers used, that with medium nitrile content (34% bound acrylonitrile) is the most important.

Experimental conditions for preparing medium grade nitrile rubber in 70-75% yield and having Mooney viscosity around 50, were standarized on a 7 kg./batch of the finished product. Storage stability of the rubber has been improved by using combination of various stabilizers. Even after 5 months of continuous aging at 60°, there was no change in gel content, Mooney viscosity number and colouration. Two samples, evaluated by users were found to be comparable to the similar imported rubbers.

Standardization of the preparation of the emulsifier required in the polymerization is being attempted. The type of the emulsifier affects the latex stability, non-linear conversion, poor reproducibility and purification of the rubber. The latex stability has been improved satisfactorily by incorporating a secondary emulsifier. Standardization of the formulation using new emulsifier composition is being actively pursued.

Negotiations with a private party are in progress for undertaking further developmental work at its factory site.

55. *Expandable polystyrene :* (ATT-34/66)

Polystyrene foam finds extensive use in low temperature insulation and packaging. One firm in the country is manufacturing this product using imported know-how. In view of the general interest of industry, attempts are being made to establish the know-how for the product.

Studies in suspension polymerization of styrene to obtain expandable polystyrene beads have been continued. With a view to overcome the lower bulk density of some of the beads, variation of interfacial tension of the suspending medium was tried. One of the suspending agent in the absence of the expanding agent, gave satisfactory results in regard to particle size, size distribution and suspension stability. Addition of expanding agent led to the particle growth to certain extent, which is responsible for lowering the bulk density of the beads. In order to minimize the quantum of lighter beads, polymerization was tried under pressure but with limited success. The effects of the design of the stirrer and the rate of stirring on the bulk density of the beads was studied. Efforts are being continued to get maximum proportion of the beads of desired size, bulk density and with good foaming characteristics.

56. *Synthetic polymers for cane juice clarification :* (ATT-86/68)

Separan AP-30, an imported product is being used by many sugar mills for the clarification of cane juice. The estimated demand of this product is about 100 T valued at Rs. 10 lakhs.

More runs for preparing the polymer in 1·5 kg./batch were carried out and further quantity was supplied to a few sugar mills for trials.

57. *Microfilters :* (ATT-87/68)

Microfilters are used abroad for a wide variety of filtrations in industry where efficient, clean and compact filtration unit is required. These products are also likely to find commercial use if indigenously available.

Filter cartridges from cotton linter pulp treated with amino resin, have been prepared and are being evaluated.

58. *Synthetic polymers for oil well drilling :* (ATT-115/68)

Oil and Natural Gas Commission has expressed an interest in development of a substitute for an imported polymeric product (Halad) which is presently used as an additive to cement in oil well drilling. This water soluble polymer when added 1% by weight of the cement, prevents quick water loss from the cement slurry and helps in proper setting of the cement. Present requirement of this product in the country is around 10 TPA valued at Rs. 4 lakhs. The demand is likely to go up to 40-50 TPA.

Halad is essentially hydroxyethylcellulose mixed with some inorganic salts. The preliminary laboratory experiments to prepare it from soda cellulose and ethylene oxide resulted in a non-uniform product. Further experiments in a jacketted sigma blade mixer using 2 kg. of the cellulose pulp gave a uniform alkali soluble product but with partial solubility in water. Preparation of hydroxyethylcellulose with higher ethoxy content is undertaken to obtain a completely water soluble product.

59. *Can lining composition :* (ATT-131/69)

Metal can lining composition based on synthetic latex are at present imported to the tune of about 100 T valued at Rs. 10 lakhs. These compositions are employed in the sealing of metal cans used for packing tinned foods, mineral oils, greases, etc.

In the light of the test reports received on the product sent out earlier to a few parties, necessary modifications were incorporated in the composition and samples sent for further trials. The performance of the composition in regard to its coating characteristics on the machine was comparable to the imported product. However, the leakage of cans at pressure of the order of 20-35 psi was reported. Steps are being taken to improve the product.

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

The work is aimed at the development of low cost water thinnable emulsion paints in place of plastic based emulsion paints.

Process parameters for the polymerization of linseed oil were studied in greater details. The emulsions, prepared from the polymerized oil, were further improved in their properties by changing the emulsifying agent. Samples of the emulsion paint with improved drying properties have been sent to a few parties for testing. Larger quantities of the product are being prepared for user trials.

61. *Polyurethane coating compositions :* (ATT-47/64)

61·1 *Water proofing composition*

Polyurethane coating composition based on shellac, castor oil and TDI was developed and found suitable for coating nylon fabric for imparting desired water proofing property. Work on the development of coating compositions for water proofing of textiles has been undertaken.

61·2 *Water repellent composition*

A similar coating composition was used for coating gum boots for export market. The coated film was tested for flexibility and was found to stand flexing upto 80,000 cycles. Negotiations are in progress regarding the release of this process to industry.

At the request of the Fiji Govt., a water repellent coating for 'Tapa cloth' was developed. Tapa cloth is made from the inner bark of the mulberry tree—*Broussonetia papyrifera.* The polyurethane coating composition was found acceptable by the Fiji Govt.

62. *Stabilizers for PVC :* (ATT-161/70)

Earlier work on the preparation of Ba-Cd PVC stabilizers was successfully completed as a sponsored project. Organo-tin compounds containing sulphur are also extensively used for the stabilization of PVC. These stabilizers impart high heat stability and give a transparent PVC product. These compounds are used for rigid PVC which will be increasingly in demand in future. Organo-tin stabilizers are being imported at present. Condensation of dibutyl tin oxide with thio acid ester are being carried out.

63. *Plasticizers for PVC (Urethane based) :* (ATT-168/70)

Recently polyurethane based plasticizers are introduced in PVC technology. These plasticizers have definite advantage over commonly used plasticizers for PVC. In future urethane based plasticizers are likely to gain considerable importance.

Preliminary work for the preparation of polyesters of different molecular weights has been undertaken. These polyesters will be used to prepare suitable plasticizers.

64. *Sulfochlorinated polyolefin elastomers (SCPE) :* (ATT-90/68)

The vulcanized SCPE rubber has several outstanding properties such as resistance to weather, heat and chemicals. These rubbers are used for lining chemical resistant storage tanks and similar plant equipment, acid hoses, hot conveyor belts and flexible steam pipes. It is also used to impart protective coating to wood, masonry fabrics, shoe soles, cables, gaskets and for packings.

On the basis of the optimized conditions, a patent entitled 'Vulcanizable graft copolymer of chlorosulfonyl-polyethylene and maleic anhydride etc., using sulfuryl chloride as sulfochlorinating agent has been applied for (Indian Patent No. 130254).

INSTRUMENTATION TECHNOLOGY

65. *ESR spectrometer :* (ATT-64/68)

This valuable instrument used extensively in analytical and research work is not manufactured in the country. Price of imported unit ranges from Rs. 2 to 3 lakhs.

A fully transistorized 100 Kc. system is being developed for achieving best possible results with high sensitivity.

This system comprises of:

1. 100 Kc. crystal controlled oscillator,
2. Calibrated, gain stabilized preamplifier,
3. Phase sensitive detector,
4. 100 Kc. power amplifier.

A magnet power supply has been completely redesigned and constructed, using chopper comparator and drift free a.c. amplifier. This modification will enhance stability and life.

Further work on control console is being continued. Following units are ready:

1. Monitor oscilloscope — This scope alongwith low frequency modulation system observes preliminary adjustments of the microwave bridge and location of resonance.
2. Recorder—Solid state (fully transistorized) recorder amplifier is developed and tested for the 10 mV sensitivity. This completes the work on flat bed recorder except the sweep circuitry.

Mechanical work of the trolley and X axis translational assembly is nearing completion.

Work on automatic frequency control for Klystron oscillator, modifications in the microwave bridge, and fabrication of sample cavity with 100 Kc. modulation facilities is being taken up.

66. *Preparative VPC :* (ATT-123/69)

Based on NCL know-how, one firm is producing vapour phase chromatographic units. The preparative assembly consisting of automatic injection and collection systems is usually attached to the parent VPC equipment. Modifications were made in collection systems as reported earlier. A high capacity injector (500 μl) was tried and found satisfactory.

Major design and developmental work on this project has been completed and fabrication of a prototype is undertaken.

67. *Direct reading spectrophotometer/colorimeter :* (ATT-169/70)

This is a very useful analytical tool for the analysis of liquid samples. The cost of a similar imported instrument ranges from Rs. 10,000 to Rs. 12,000. This instrument is mostly used in the quality control laboratories of chemical and drug industries and also in clinical laboratories.

The instrument developed in the NCL uses a solid state amplifier and all the components including grating are indigenously available. The following specifications, have been achieved and the instrument is comparable to the imported instrument 'Bausch and Lomb-Spectronic 20'.

Specifications :

Wavelength range	...	350-700 mμ
Photometric reproducibility	...	± 1 % full scale
Reflectance	...	
Monochromotor	...	Grating with 15,000 lines/inch

68. *D. C. recording polarograph :* (ATT-134/69)

The project aims at designing and fabrication of D. C. recording polarograph. Polarographs having desirable sensitivity are not being produced in the country. The demand for this equipment in the next few years is estimated to be 1000 units.

Development work on this equipment has been completed and one prototype has been fabricated. Our unit is found to be comparable with the imported Sargent Model XXV polarograph.

Specifications achieved :

Sensitivity	...	0·003 μa per mm. to 1·4 μa per mm. in 20 ranges.
Time required for one complete bridge rotation	...	20 minutes
Full deflection of the recorder	...	2·5 mV
Response time of the recorder	...	10 seconds
Chart speed of the recorder	...	40 inches per hour.

Extensive performance tests are being carried out to ensure reproducibility and reliability after which the know-how will be offered to industry.

69. *Ultrasonic interferometer :* (ATT 124/69)

The details of the design of a prototype of this instrument has been worked out. Attempts will be made to release the designs and the fabrication know-how to industry.

The project is now concluded.

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RESEARCH PROJECTS

1. STUDIES IN SOLID STATE

1·1 *Studies on spinels :* (B-1.10/68)

When the tetrahedral A sites of a spinel structure are occupied by diamagnetic ions, the 90° B-B interactions become quite significant. The Cr^{3+}—Cr^{3+} interactions in chromites are known to be antiferromagnetic whereas the Mn^{4+}—Mn^{4+} interactions in manganites are known to be ferromagnetic. In order to investigate their difference in the behaviour of isoelectronic ions Cr^{3+} and Mn^{4+} with a $3d^3$ configuration, ,compounds containing diamagnetic ions at tetrahedral sites and Mn^{4+} and Cr^{3+} ions at octahedral sites have been prepared.

The work is divided into two systems. The first system compounds contain Li^{1+} and Zn^{2+} at tetrahedral sites and Mn^{4+}, Cr^{3+} and Li^{1+} at octahedral sites. The second system compounds contain Li^{1+}, Zn^{2+} and Cu^{1+} at tetrahedral sites and Mn^{4+}, Cr^{3+} and Mg^{2+} at octahedral sites. The compounds were prepared by mixing the oxides under alcohol and firing mixture in oxygen atmosphere at 800°, 900° and 950° with intermediate cooling and grinding.

The completion of the reaction was checked by X-ray diffraction studies and all compounds showed cubic spinel structure. Paramagnetic susceptibility of all the compounds has been measured by the Guoy method in the temperature range 80°—600°k and $\frac{1}{X_m}$ was plotted as a function of temperature. The θ values were calculated and it was observed that there is a gradual transition from ferromagnetic behaviour to antiferromagnetic behaviour, as the concentration of Cr^{3+} is increased or the concentration of Mn^{4+} is decreased.

It has been conlcuded that the reason for the difference in behaviour of Cr^{3+} and Mn^{4+} lies in the difference in the radial extension of the orbital wave functions of the two ions.

The electrical conductivity of the pellets has been measured at various temperatures from room temperature to about 300°. It is observed that the activation energies of compounds containing copper are less than the activation energies of the compounds which do not contain copper.

1·2 *Studies on photoconducting materials :* (AB-5/62)

Photoconducting materials form an important field of investigation in solid state chemistry. Large number of commercial devices are based on these materials. Recent interest in oxide glasses and electrical devices based on chalcogenide glasses has shown promise in this field. The project is aimed at investigation of new processes, techniques for production of photoconducting materials such as layers, thin films or crystals for use in devices.

Heterojunctions of *p*-type PbS on n-type CdS chemically and vacuum deposited thin layers and crystals and Cu on CdS crystal were fabricated. These heterojunctions show non-linear I-V behaviour and are also photosensitive. The photoresponse has been recorded as a function of illumination and temperature.

A new instrument for automatic recording of current voltage curves for heterojunction devices was fabricated in prototype form. This has now to be made in a panel form.

Electroluminescent phosphors for use in image conversion devices have been synthesized and the characteristics have been measured.

1·3. *Studies on ferroelectric glasses :* (B-2·6/70)

Vanadium oxide glasses containing thallium were prepared and the electrical and optical properties studied. Some of the glasses showed very pronounced ferroelectricity. Ferroelectricity in glasses seems to have been observed for the first time. Some typical compositions where ferroelectricity has been observed are:

	V_2O_5	P_2O_5	Tl_2O_3	
A	40	40	20	weight %
B	50	40	10	
C	60	30	10	

The dielectric constant at room temperature for one of the compositions is 1561, curie temperature 62° and has spontaneous polarisation of 0·10 micro coulombs/cm^2.

The electrical conductivity of the glass is highly sensitive to infra-red radiation. These properties are being further investigated.

Some compositions without thallium oxide were also found to be ferroelectric. On investigating the $V_2O_5 — P_2O_5$ system further it was found that the 50 : 50 wt. % composition showed the best ferroelectric properties. Dielectric constant values of these glasses were in the range of 20-50.

These glasses were found to be water soluble and the crystallized out substance was also found to be ferroelectric. The curie temperature was 164°. The dielectric constant of the crystallized phase is 20 and the spontaneous polarization 1·0 μC/cm^2.

The glass formed on melting the crystallized substance had the same properties as the crystals.

1·4 *Dielectric properties and molecular structure of organic compounds :* (B-2·6/69)

The dielectric properties of long chain organic compounds yield useful information regarding their molecular structures.

From the dielectric constant, density and refractive index measurements the dipole moments of a series of n-long chain alkoxy ethanols and propanols were evaluated as a function of temperature. The dipole moment data indicated that these compounds exist as intermolecularly hydrogen bonded dimers in the gauche form. These structures are in conformity with the infrared analysis. A similar study was undertaken in the case of a series of a long chain alcohols.

2. THIN FILMS

2·1 *Structure of thin films :* (B-4·3/58)

Electron diffraction studies were carried out on vacuum deposited films of various alloys viz., In-Pb, Sb-Sn, Sb-Cd, Sb_2Tl_7 and also on some oxides with special reference to the crystal growth, epitaxy, phase transition and their orientation relationships with the substrates. In the case of In-Pb system two f.c.c. phases (a_o = 4·98 A° and 6·04 A°) were observed at lower and higher substrate temperatures. For In-Sn system three different phases were observed. Two of which were not reported hitherto were tetragonal (a_o = 5·12 A°; c_o = 5·48 A°; a_o = 3·99 A° and c_o = 2·56 A°). All these grew epitaxially at appropriate orientations on single crystal substrates. Deposits from Cd-Sb alloy formed by vapour phase deposition consisted mostly of Cd phase at a lower substrate temperature of Cd-Sb (orthorhombic) at an intermediate and Sb at higher temperatures. Deposits of the Sb_2Tl_7 having an f.c.c. structure (a_o = 11·57 A°) grew with parallel orientation on a cube face of Nacl. When In-Cd alloy was vacuum deposited, the films consisted mostly of In_2O_3 developing different orientations on different faces of rocksalts.

Density or blackening characteristics of photographic films (ORWO FO 6) for electron diffraction work was evaluated and it was found that the density ranging between 0·2 and 0·8 followed the rectilinear law of blackening with high electron beam energy.

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

The work on thin film thermistor was continued with variations of compositions and methods of preparations. Different samples were prepared from vapour phase and their resistance measured between –100° and +100°. TCR varied from 0·5 to 3·5% depending on the preparation of the films, subsequent heat treatment, etc. Electrical properties such as conductivity, resistivity, TCR, Hall effects, etc., were measured for many oxidic deposited films and results are being evaluated. A new set-up for measurements of Hall effect at a low temperature in the region of liquid nitrogen, was designed and measurements are being made for various semi-conducting films. A new equipment working on the principle of multiple beam interferometry, was designed and set up for measuring film thickness of vapour phase deposits.

A preliminary study was made on dielectric properties of zinc sulphide films formed at room as well as higher substrate temperatures with varying film thickness. It was found that dielectric constant changed, though slowly-with substrate temperature as well as film thickness. Different capacitors were prepared and their break-down voltages are also being measured.

Optical properties of metallic and semi-conducting films are being studied with a newly designed instrument. Reflections as well as transmission coefficients of these films were measured using a polarized light for various angles of incidence as well as wave lengths. The effects of film thickness on adsorption coefficients and also on refractive index were also studied. It was found that both R_S and R_P varied with film thickness. For chromium films refractive index 'n' decreased slowly with the increase of film thickness, then increased, ultimately assuming a constant value similar to the bulk value with a further increase of film thickness.

3. NUCLEAR AND RADIATION CHEMISTRY

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

In continuation of earlier studies on the application of Mössbauer spectroscopy, studies were undertaken to determine the direction of electric field gradient in normal spinels $Zn[Fe_2]O_4$ and $Cd\,[Fe_2]O_4$. Mössbauer spectra of both $Zn\,[Fe_2]O_4$ and $Cd\,[Fe_2]O_4$ were similar and had distinct quadrupole splittings of 0·36 and 0·79 mm/sec., respectively at 25°. The Mössbauer spectra of solid solutions of these two spinels showed a monotonic increase in the magnitude of the quadrupole splitting on increasing the percentage of $Cd\,[Fe_2]\,O_4$ in the solid solutions of $Zn\,[Fe_2]\,O_4 + Cd\,[Fe_2]O_4$. This indicated that the signs of the electric field gradients at the B sites in $Zn[Fe_2]\,O_4$ and $Cd\,[Fe_2]\,O_4$ are the same and not opposite as suggested by the calculations of Hudson and Whitfield (A. Hudson and H. J. Whitfield, *Molec. Phys.*, *12* ,165, 1967), because in the latter case the magnitude of quadrupole splitting should have passed through a minimum as the percentage of Cd [Fe_2] O_4 was progressively changed in the solid solution from zero to pure Cd [Fe_2]O_4. It has been shown that the source of error in the theoretical calculations of Hudson and Whitfield is their use of inaccurate 'u' parameters for Zn [Fe_2]O_4 =0·385 A° and Cd [Fe_2] O_4 =0·393 A°. These values should, instead, be taken as 0·380 A° and 0·386 A° respectively (P. K. Baltzer, P. J. Wojtowicz, M. Robbins and E. Lopatin, *Phys. Rev.*, *151*, 367, 1966).

3·2 *Radiolysis :* (B-3·3/67)

3·2·1 *Temperature effects in the radiation chemistry of water :* A study of γ-radiolysis of the aerated and deaerated ferrous sulphate systems and the ceric sulphate system over a wide range of temperature showed that the primary yields of H and OH radicals and hydrogen peroxide are constant from 0° to 120°. This result indicates that the radical diffusion model for radiolysis of liquids, now widely accepted, needs to be changed.

3·2·2 *Temperature effects in the radiation chemistry of the aqueous benzene system :* All the details of the mechanism of the reaction of OH radicals with benzene were revealed by a study of this system. Phenol and the two isomeric (α and β) hydroxymucondialdehydes were formed in the reaction. Methods of analysis for these compounds were developed. The sum of the yields of three products which is equal to G(OH) is constant upto 60°. Beyond this temperature, the phenol yield rises sharply indicating the possible occurrence of the reaction.

$$H + O_2 \rightarrow OH + O$$

At 220° G (phenol) = 5

3·2·3 *Photochemistry of H_2O_2 solutions in presence of benzene :* This study had confirmed the above mechanism of reaction of OH with benzene. Phenol and hydroxymucondialdehyde were formed in the photolysis exactly as in the γ radiolysis. Roughly one out of every ten H_2O_2 molecules decomposing, seemed to break up into OH radicals. The rest of the decomposition of H_2O_2 is presumably along a molecular mechanism giving H_2O and O_2 directly.

3·2·4 *Photochemical hydroxylation of benzene in presence of ferric ions :* In presence of ferric perchlorate easily measurable concentrations of phenol, were formed in aqueous benzene solutions exposed to UV even at a low dose. There was however, no hydroxy-mucondialdehyde formed. It indicates that the mechanism of phenol formation involves something besides the OH radical.

4. THERMODYNAMIC STUDIES

4·1 *Studies on phase equilibria :* (B-3·6/70)

4·1·1 *Thermodynamic properties of binary systems :* A modified 'Gillespe still' was set up so that studies on vapour-liquid equilibria can be undertaken under both isobaric and isothermal conditions. Necessary analytical facilities for the determination of composition of the vapour and liquid fractions, by measurement of density, refractive index or VPC analysis, were created. Experiments on the vapour-liquid equilibrium on ethyl alcohol and water mixtures over the entire concentration range gave results which satisfy the tests of thermodynamic consistency.

A twin type calorimeter similar to that described by Adcock, A. D. and McGlashen, M. L. (*Proc. Roy. Soc., 226A*, 266, 1954), was assembled for measurement of heats of mixing of liquids. In this calorimeter provision was made to compensate for the heat of the reaction by supplying electrically an equivalent quantity of heat to the reference vessel for exothermic reactions and to the reaction vessel for endothermic reaction. Vapour space was completely eliminated and yet provision was made for the expansion or the contraction of liquids on mixing. The apparatus was tested by measurements of the heats of mixing of methyl alcohol and water over the entire range of composition and gave results in very good agreement with those available in the literature.

4·1·2 *Heat capacity of solids :* A calorimeter for measurement of heat capacity of solids from room temperature to 500° (expected) was partly constructed. This was designed so as to be an adiabatic intermittent heating calorimeter. It consists of a silver vessel (10 cm. dia. × 90 cm.) with internal silver-vanes for better heat conduction. It weighs about 150 g. and has arrangement for heating by means of 36 SWG platinum wire wound around it. This was suspended in an inner radiation shield of silver which in turn was suspended into an outer radiation shield, which again was suspended in an outer brass can. The whole assembly was enclosed in a metal can capable of being evacuated to a vacuum of 10^{-5} mm of Hg. Temperature of the calorimeter vessel, inner and outer radiation shields and outer brass can would be measured by chromel-alumel thermocouples which was already calibrated at the following temeperatures : (i) melting point of ice, (ii) boiling point of water, (iii) melting points of tin, zinc and cadmium metals.

4·2 *Thermochemical studies :* (B-3·7/70)

Thermodynamic functions for the formation of Cu (II) and Ni (II) complexes of β-diketones, viz., acetylacetone (HAcAc), benzoylacetone (HBzAc), anisoylacetone (HAyAc) and dibenzoylmethane (HBzBz) in 75 volume percent dioxane + 25 volume percent water were determined. The enthalpy ($\triangle H$) and the free energy ($\triangle G$) changes increase in the following order :

$$\text{HBzBz} > \text{HAyAc} > \text{HBzAc} > \text{HAcAc}$$

The phenyl ring in the substituted acetylacetones (i.e., HBzBz, HAyAc and HBzAc) acts as an electron donor and leads to a higher electron density at the oxygen atoms in the β-diketones and hence the formation of more covalent oxygen to metal bonds. The presence of a strongly electropositive OCH_3 group in the phenyl ring of HAyAc further increases by induction the donor property of the oxygen atoms in this ligand as compared to HBzAc and hence forms stronger O-M bonds in its complexes as shown by the order of $-\triangle H$.

The thermodynamic functions $\triangle X^\circ$ ($X = G$, H, S) were separated into two parts (a) $\triangle X^\circ_c$, temperature independent component intrinsic to the molecules or ions and arising out of short range or covalent forces insensitive to the environment (b) $\triangle X^\circ_{el}$ temperature dependent part, owing to to the interaction of the dipoles or ions with long range electrostatic forces in the solvent medium, thus, $\triangle X^\circ = \triangle X^\circ_c + \triangle X^\circ_{el}$. The increase in the magnitude of the free energy ($\triangle G^\circ$) and the entropy ($\triangle S^\circ$) changes and a decrease in the magnitude of enthalpy ($\triangle H^\circ$) change for the formation of *bis*-β-diketonato Cu (II) and Ni (II) complexes in water-dioxane medium as compared to that of water was shown to arise out of the differences between the electrostatic interactions of the metal ions and the ligand anions in the two media. A calculation based on the Born model of charged ions, that the electrostatic interaction between the metal cations and the ligand anions should lead to an endothermic contribution from $\triangle H^\circ_{el}$ to the total enthalpy change $\triangle H^\circ$. In agreement with this conclusion, a good agreement was obtained between the calculated values of $\triangle H^\circ_c$ for the formation of *bis*-acetylacetonato-Ni (II) in 75 volume per cent dioxane+25 volume per cent water in 100 percent water media.

4·3 *Thermodynamic properties of solutions :* (B-13·263)

Ultrasonics is a powerful means for studying the properties of solutions and the nature of coulombic attraction. Since polyelectrolytes possess both electrolytic as well as chain molecular properties, adiabatic compressibility measurements for the same are expected to give interesting results.

Some polyelectrolytes such as polymethacrylic acid, polymethacrylamide and others were studied earlier. The work has been extended to polyacrylic acid and polyacrylamide as these are structurally closely related to the above polymers and all of them have functional groups which can form hydrogen bonded structure.

The adiabatic compressibility of polyacrylic acid and polyacrylamide alongwith their corresponding monomers and two polysodium acrylates obtained by neutralizing the polyacid to 25% and 100 % with sodium hydroxide have been investigated. The total adiabatic compressibility of polyacrylic acid solution is higher than that of the corresponding salt solutions or of polyacrylamide solutions. The unneutralized acid does not dissociate much even in dilute solution and the magnitude of electrostriction in polyamide is greater than in acid. The ϕV_2 and ϕK_2 values for monomers and polymers are seen almost concentration independent and so also are seen for the results of sodium salts of polyacid. In 100% neutralized polyacid, the dissociation of counter ions are complete and the magnitude of electrostriction is highest in this case. Accrodingly, lowest ϕV_2 and ϕK_2 values (37·0 cc/mole and -50·50 × 10^{-4} cc/bar/mole) are obtained. However, the dissociation and therefore the magnitude of electrostriction is somewhat reduced in presence of 1·0 M NaCl solution and accordingly the values increased to 42·80 cc/mole and 83·0 × 10^{-4} cc/bar/mole respectively. Some amphoteric polyectrolytes are being synthesized for further work in this line.

5. TRANSPORT PROPERTIES

5·1 *Isotopic effect for the diffusion of ^{57}Co and ^{60}Co in copper :*
(B-2·1/67)

The correlation factor 'f' in solid state diffusion depends only on the mechanism of diffusion and the crystal structure and in the case of impurity diffusion on the relative jump rates. The value of the correlation factor 'f' is therefore useful in identifying the mechanism of diffusion in solids. The values of 'f' can be obtained from accurate measurements on the relative diffusion rates, D_α and D_β of the two different isotopes α and β of the same element with masses m_α and m_β respectively viz.

$$f = \frac{1 - (D_\alpha / D_\beta)}{1 - [\{(n-1)m + m_\beta\} / \{(n-1)m + m_\alpha\}]^{\frac{1}{2}}} \quad \ldots\ldots (i)$$

where m is the mass of the solvent atom and n is the number of atoms involved in the diffusion process. Simultaneous diffusion of ^{60}Co and ^{57}Co in Cu metal was carried out at three temperatures in the interval 890°-1040°. The values of $[1-(D_{60}/D_{57})]$ determined by equation (i) from the calculated values of the correlation factor for different diffusion mechanisms in the face centered cubic lattice of copper and those experimentally determined are shown in the following table. It would be observed that the average experimental value of 0·01903 for [1-(D_{60}/D_{57})] is in close agreement with that derived for the vacancy mechanism. This indicates that the diffusion mechanisms such as interestitial, interstitialcy, exchange and 4-ring mechanisms could be ruled out for the diffusion of cobalt and copper.

Table : Theoretical and experimental values of [1-(D_{60}/D_{57})] for the diffusion of cobalt and copper

Machanism of diffusion	Correlation factor 'f'	[1-(D_{60}/D_{57})]	
		Calculated	Experimental (890°-1040°)
Interstitial	1·0000	0·0253	0·01903 ± 0·01
Vacancy	0·7815	0.0198	
Exchange	1·0000	0·0122	
Interstitialcy	0·8000	0·0098	
4-Ring	1·0000	0·0060	

5·2. *Diffusion studies in liquid :* · (B-3·8/70)

A sintered glass diaphragm diffusion cell with magnetic stirring arrangement has been assembled. The apparatus has been standardized by determining cell constants at 25°, 30° and 35° and the diffusion coefficients of KCl in the concentration range 0·01M to 2M KCl.

6. CRYSTAL AND MOLECULAR PROPERTIES

6·1. *Crystallography :* (B-2.5/59)

The precise structure of *o*-monomethylaminobenzoic acid was determined with the help of about 950 X-ray reflexions, and a thorough refinement of the structure of *p*-nitrobenzoic acid was completed with the help of about 750 X-ray reflexions.

Crystals of *o*-monomethylaminobenzoic acid are monoclinic, space group $P\frac{21}{C}$ with a = 8·15 Å, b = 15·09 Å, c = 7·02 Å:

$\beta = 118.3°$; ρ_o, 1.307 g. cm^{-3} and ρ_c for Z = 4, 1.319 g. cm^{-3}. The molecules as usual form dimers; there is an intramolecular NH......O hydrogen bond of length 2·67 Å; as well in the molecule. The C-N bond is shortened from its single bond value of 1·48 Å to 1·37 Å thereby suggesting strong conjugation of the monomethylamino group with the benzene ring.

In the refined structure of *p*-nitrobenzoic acid, the central aromatic bonds are of lengths 1·381 ± 0·006 Å and 1·384 ± 0·006 Å these lengths are shortened from the normal value in crystalline benzene (1·393 Å) although the shortening is still more in *p*-nitroaniline and *p*-aminobenzoic acid. These results indicate that cooperative electronic interaction between the para substituents in the latter compounds must be only partly responsible for the shortening of the central aromatic bonds.

In the above structures thermal anisotropy was also studied. In both the structures, the carboxylic group was found to oscillate about the C-C bond with an r.m.s. amplitude of about 9°; the corresponding value in the structure of *p*-toluic acid was 12°.

Structure analyses of 2-nitro, 4-methylbenzoic acid and 2-nitro, 5-methylbenzoic acid were still in progress; the structure analysis of *o*-dimethylamino benzoic acid was also started.

7. SYNTHETIC INORGANIC CHEMISTRY

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

In the process of synthesizing new oxo-titanium organics, the reactions studied during the year were principally with *bis*-cyclopentadiene dichlorotitanium, itself a π-bonded organotitanium species. Dialkoxides of Ti (IV) attached to aromatic ligands reacted to give both monochloro and chlorine-free oxotitanium complexes, though difficulty was experienced in getting good yields and in isolation of some products in a state of purity. The monochloro product is a reactive solid, further reactions of which are under study. An attempt to introduce a Ti-C sigam bond by reaction with lithium phenyl was not successful so far.

In the newly synthesized *bis*-chelated dichlorotins, the chlorine atoms were found less reactive than in the alkyl/aryl chlorotins. The former compounds failed to react with Grignard reagents or lithium organics, but the latter ones reacted. Chelated organotins were prepared from alkyl/aryl chlorotins and ligands in presence of sodium ethoxide. These substances were coloured and stable and those which dissolved in benzene were found to be monomeric in boiling benzene. Their IR spectra were of the expected type, suggesting that the ligands were coordinated through the carbonyl group to the tin atom.

Chelated tin^{II} compounds of the type L_2Sn, prepared from stannous chloride, the ligand (LH) and sodium ethoxide, were coloured stable substances. These reduced ferric ion to ferrous and were decomposed with hydrogen sulphide. In non-aqueous medium these reacted with chlorine, bromine and iodine forming the dihalides, L_2SnX_2.

Attempts are being made to react triphenyltin sodium with chelated chlorotitanium (IV) to synthesize and study the compounds containing Ti (IV)-Sn(IV) bonds.

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

7·2·1 *Reactivity of coordinated ligands:* The reactivity of a number of coordinated β-dicarbonyl compounds and oximes were previously examined. In continuation, chelates of 2-hydroxy-l-naphthaldoxime and 5-nitro-β-resorcylaldoxime with Cu(II), Co(II), Ni(II), Zn(II), Pd(II) and Be(II) have been prepared and their reactivity examined. Only the copper and beryllium chelates of either ligand could be acetylated. Encouraged by the successful acetylation of these copper and beryllium chelates, acetylation of copper chelates of 5-nitrosalicylaldoxime and 5-bromosalicylaldoxime was successfully achieved.

E.D.T.A. chelates of Cu(II), Co(II), Ni(II) and Nd(III) have been prepared in a pure state through ligand replacement from the metal chelates of 2-hydroxy-l-naphthaldehyde.

Pure complexes of rare earth metals (La, Ce, Pr, Nd, Sm) with 2-hydroxy-l-naphthaldehyde have also been prepared, so that their reactivity could be examined.

7·2·2 NMR *spectroscopic studies on metal chelates :* NMR spectra of beryllium (II) chelates of 1, 3-diphenyl-propanedione, l-phenyl-l, 3-butanedione, 2, 5-dimethoxy-4-chloroacetoacetanilide, *o*-chloroacetoacetanilide, and the corresponding brominated chelates have been recorded in deutero-chloroform. Absence of signal due to ring-hydrogen in the brominated chelates provided evidence for the replacement of the ring-hydrogen by bromine.

7·2·3 *Mass spectrometric studies on metal chelates :* Elucidation of structure of metal complexes through mass spectrometry is still a relatively new approach. It was of interest to study the mass spectra of the above beryllium chelates (cf 6·2·2) to study the decomposition pattern of coordinated ligands. The spectra of all the compounds showed well-defined molecular ions, and fragment corresponding to the loss of a ligand. Bromine and chlorine atoms in the ions could be easily recognised from their isotopic patterns. The information gained from this study should prove useful in the structure elucition of unknown metal chelates.

Recent reports on the potential applications of certain cyclopentadienyl metal complexes have stimulated researches on such compounds considerably. As a part of the work on the synthesis and studies of mixed complexes of cyclopentadienyl and sulpur-containing ligands with titanium, the reactions of *bis* (cyclopentadienyl) ethoxytitanium chloride, $(C_5H_5)_2$ $Ti(OC_2H_5)Cl$, and of cyclopentadienylethoxytitanium dichloride $C_5H_5Ti(OC_2H_5)Cl_2$, with thiophenol and anhydrous ammonia were examined. Whereas the reaction of the monochloro compound yielded the stable compound $(C_5H_5)_2Ti(SPh)_2$, that of the dichloro compound gave only an unstable product. Attempts were also made to synthesize cyclopentadienyltitanium complexes with phosphorus containing ligands. *Bis*(cyclopentadienyl) titanium dichloride was found to undergo reactions with tributyl-phosphate and diethylphosphite at about 150°-160° yielding products of indeterminate compositions.

Attempts to synthesize mixed cyclopentadienylzirconium complexes containing thiosalicylato and ethane-1, 2-dithiolato groups (similar to the titanium ones reported earlier) failed to give stable products. *Bis*(cyclopentadienyl) zirconium dichloride for the purpose was prepared by reacting zirconium tetrachloride with thallium cyclopentadienide—a new route to synthesis. Attempted substitution of the chloro group in zirconium chelates L_3ZrCl (LH = benzoylacetone or dibenzoylmethane) with cyclopentadienyl group, through reaction with thallium cyclopentadienide, resulted only in yielding ZrL_4 chelates. A pure reaction product could not be isolated from the reaction of *bis*(methylsalicylato) zirconium dichloride or *bis*(acetyl-acetonato) tin dichloride with thallium cyclopentadienide.

7·3 *Fluorine chemistry :* (B-6·4/69)

The minor constituent in the mixture of isomeric dibromobenzotrifluorides (obtained from mercurated products) has been identified as 3,4-dibromobenzo trifluoride. This was done by synthesizing this particular isomer by a new route. Earlier the constituent was shown to be different in its NMR spectrum from 2, 5-dibromobenzotrifluoride (prepared according to methods reported in the literature). Benzotrifluoride was mercurated in the *m*-position by the reaction of the Grignard prepared from *m*-bromobenzotrifluoride with mercuric chloride. C, H analysis of the solid reaction product of fluoral hydrate and acetylacetone agrees with the cylic structure having molecular weight 220. NMR, IR and UV spectra also agree with this. The liquid product is under investigation.

Attempts to directly acetylate benzotrifluoride in presence of catalysts have so far been unsuccessful.

Study of the UV spectra of trifluoromethyl derivative of cupferron shows that the tautomeric equilibrium is probably not affected by presence of ammonium citrate. However, it is possible that some of the intermediates in the reduction of the compound at the dropping mercury cathode may be preferentially stabilized by citrate. The UV spectrum of trifluoromethyl dithizone shows surprisingly a lowered absorbance compared to ordinary dithizone.

The sample of sodium silicofluoride sent by a firm in Madras was tested for its suitability for cryolite manufacture. It was, however, found that the material exhibited poor reactivity to soda ash, resulting in low yields of sodium fluoride.

8. PHYSICO-ANALYTICAL CHEMISTRY

8·1 *New analytical reactions :* (AB-16, --,

8·1·1 *Sulphosalicylic acid in analytical chemistry :* It was indicated earlier that the polarograms of cobalt (III)and copper (II) in sulphosalicyclic acid exhibited a pronounced minima and therefore were of limited use in analysis. The minima was ascribed to electrostatic repulsion between the negatively charged depolariser and the micro-electrode. The mixed chelate of cobalt (III) with pyridine and sulphosalicylate on the other hand is free from polarographic minima. The effect of varying concentrations of pyridine in the sulphosalicylate supporting electrolyte on the polarographic minima indicates that the suppression of the minima cannot be attributed to the pyridine adsorption on the electrode. Perhaps the mixed chelate orients with its pyridine residue closes to the electrode; the pyridine which acquires a$\delta+$ charge by electron donation to the metal may act as a bridge for electron transfer from the electrode to the chelate.

The absence of minima in the polarograms of the 1:2 sulphosalicylate chelates of zinc and nickel underlines the fact that a multiple negative charge is not the sole prerequisite for the occurrence of polarographic minima. The single well-developed, quasi reversible cathodic step of zinc breaks into two or more steps in the higher pH region (>8). The effect of pH and of ligand concentration suggests participation of hydroxyl ions in coordination with increasing pH.

Many metal cations in their lower oxidation states chemically reduce oxidants such as chlorate, perchlorate and nitrate at the d.m.e. In presence of an excess of the oxidant, there is a cyclic regeneration of metal cations in their higher oxidation state. This gives rise to catalytic waves. In complex forming supporting electrolytes the catalytic current is decreased in proportion to the extent the cation in the lower oxidation state participates in complex formation. The decrease in such catalytic currents has been taken advantage of in evaluating the formation constants of the chelates of titanium (III) and molybdenum (III) with sulphosalicylate. Evaluation by conventional methods is beset with experimental difficulties arising from the instability of these lower-valent cations.

8·1·2 *Redox behaviour of coordinated ligands :* It was indicated that chelation of a metal cation to a polarographically active coordinating group not only affects the redox potential of the chelated ligand but also sometimes influences the pathway and the product of reduction as well. The change in the redox potential is not restricted to polarographically active coordination sites only. Even when a group other than the coordinating group is electroactive, the effect of coordination is relayed to such groups. For instance, the chelates of cobalt (II) and iron(II) with 5-nitro 1,10-phenanthroline are reduced at potentials more positive than the parent ligand. The $\triangle E_{1/2}$ for the ferrous chelate is greater than that for the cobaltous chelate presumably because of the greater stability of the former chelate.

These effects which cannot be explained readily without a quantitative picture of the electron density in a chelated molecule have, however, useful practical applications. Metals such as the lanthanides, aluminium, calcium, magnesium etc., which do not readily lend themselves to conventional polarographic analysis owing to their highly negative half-wave potentials, can be analysed by measuring the diffusion currents of the respective chelated ligands. Furthermore, when the steps of the chelated ligands and the free ligand are non-kinetic in nature, the necessary parameters for evaluating the stepwise formation constants of these chelates become available. Simple equations have been set up relating the formation constants to the diffusion currents. The validity of this new approach has been verified by evaluating stepwise formation constants of the chelates of iron(II) and nickel(II) with nitroso-R-salt, of iron(II) with nioxime and of magnesium with calmagite. The figures obtained are closely comparable with those obtained by the more orthodox potentiometric methods.

9. NATURAL ORGANIC PRODUCTS

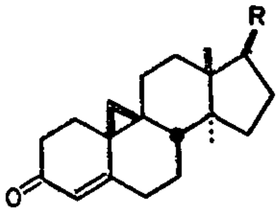
9·1 *Celastrus paniculatus :* (AB-18/67)

The work has been undertaken to isolate and study the pure polyesters from *Celastrus paniculatus* (Hindi-Malkangini) which possess antifertility activity and to elucidate the structure of the individual polyesters.

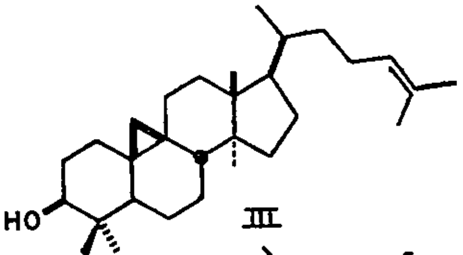
The isolation and structure elucidation of individual polyesters is under progress. The total esters have been hydrolysed to polyalcohols and then chromatographed by using different adsorbents and solvent systems.

9·2 *Utilization of the by-products of opium alkaloid industry* : (AB-21/67)

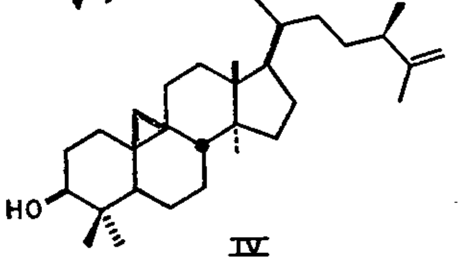
The objective of this project is to prepare hitherto unknown 9, 19-cyclosteroid hormones (I and II) from the triterpenes cycloartenol (III), cyclolaudenol (IV) and to evaluate their biological importance. These triterpenes (III and IV) are now readily accessible from non-saponifiable fraction of opium marc - a waste product of the Indian opium alkaloid industry.



I R = $-COCH_3$
II R = $=O$

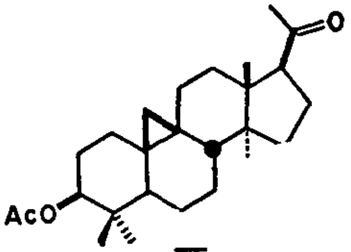


III

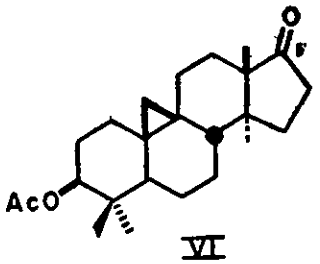


IV

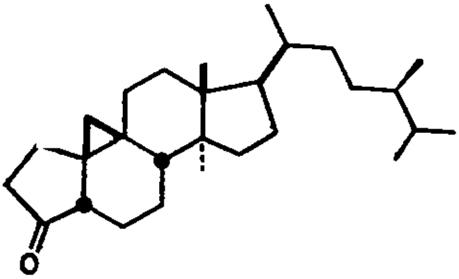
As a first step towards this objective a novel sequence of reactions were employed for the degradation of the side-chain of (III) and (IV). Thus C_{17}-methylketone (V) and C_{17}-ketone (VI) have been obtained in excellent yields. Likewise ring A modification has also been separately completed upto A-nor-*cis* hydrindanone (VII). The conversion of (VII) into (VIII) is in progress.



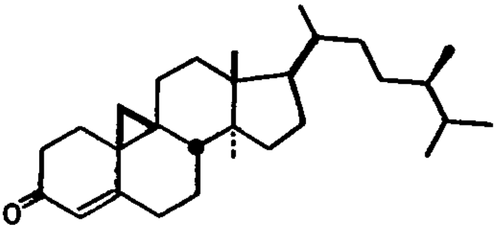
V



VI



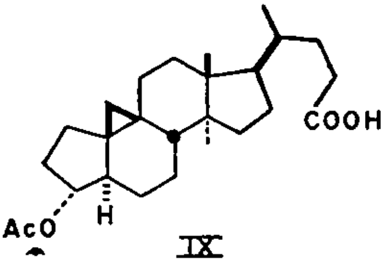
VII



VIII

As yields in the modification of ring A have not been good, another set of reactions is being investigated to achieve the above objective viz., conversion of 3β-hydroxy-4, 4-gemdimethyl system of ring A into 3-oxo-4-ene-system characteristic of many naturally occurring steroid hormones.

Another scheme which suitably combines, the above set of reactions is also under investigation. Thus, the acetate-acid (IX) has been obtained from cycloartenol in fairly good yields. Further work for converting (IX) into (I) and (II) is in progress.



IX

9·3 *Compounds of vegetable origin for insect control:* (AB-74/69)

Under this project it is proposed to investigate some of the Indian plants which are known to possess some insect repellent and insecticidal activities and to identify new compounds which may serve as basis for developing new types of synthetic pesticides, insecticides etc.

Individual constituents of extract from the wood of *Cedrus deodara* were tested for juvenile hormone activity against red cotton bug. Maximum activity was shown by the whole extract followed by β-himachalene oxide, total ketones, total alcohols and ∝- and β-himachalene in decreasing order. Report on the activities of the constituents of the extract from *Gardenia lucida* (oleoresin), *Dipterocarpus pilosus* (essential oil), *Cassia fistula* (petrol ether extract of rind bark), and epishellolic and jalaric acids is awaited.

Chromatographic separation of the petroleum ether extract and that of chloroform extract of *Spilanthes oleraceae* was carried out on a bigger scale to get the pure compounds indicated to be present earlier. Out of the three crystalline compounds obtained, two appear to be known (though reported from a different source) while the third appears to be a new one. All are amides of long chain unsaturated acids. Work is in progress on their chemical characterization.

The total extract of *Cedrus deodara* Loud was also separated into acidic and neutral fractions. Little or no activity was shown by the neutral fraction. Attention was therefore turned to the acidic fraction in which the activity appeared to be confined. In order to isolate individual acidic components possesing juvenile hormone activity, the total acids were converted into methyl esters. Work on the separation of the methyl esters is in progress.

9·4 *Paspalum scrobiculatum* (*Marathi—Harik*) *:* (AB-89/70)

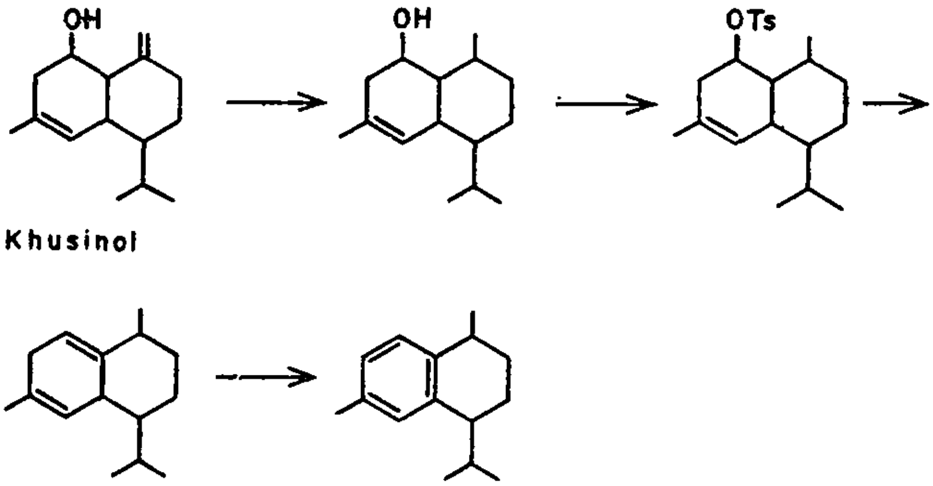
Alcohol extract of a fungus grown on Harik has been claimed to possess important tranquillizing activity. This extract has been further processed to isolate the active components. The two components present in the extract have been separated by preparative thin-layer chromatography and the major component sent for testing its physiological activity. The preliminary reports indicate that it possesses tranquillizing activity. Further investigation of the compound is in progress.

This work is being carried out in collaboration with Indian Drug Research Association, Poona.

9·5 *Vetiveria zizanoides :* (B-7.4/60)

Stereochemically pure (+) calamenene (α, + 37°) was synthesized from khusinol by the following sequence of reaction.

Khusinol was hydrogenated with PtO_2/EtOH to give dihydrokhusinol which on treatment with *p*-toluene sulphonyl chloride in pyridine gave the corresponding tosyl derivative. This tosyl derivative was heated in presence of a base (pyridine) under nitrogen atmosphere. The product obtained was finally dehydrogenated with tetrachloro-*o*-benzoquinone to give (+) calamenene.


Khusinol

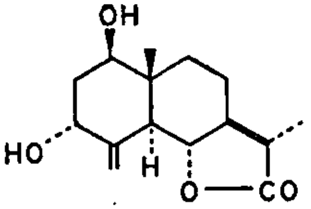
(+)-Calamenene

Synthesis of α-calinene is in progress.

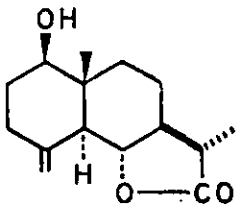
10. SYNTHETIC ORGANIC CHEMISTRY

10·1 *Transformation products of costunolide :* (B-8.15/66)

A 1, 3-dihydroxysant-4(15)-enolide (IV), structurally related to natural Erivanin, isolated from *Artemesia fragrans*, was prepared from dihydrocostunolide via dihydroreynosin (V).



IV



V

10·2 *Chemical transformations of dehydrocostus lactone :* (B-8·19/65)

Dihydrodehydrocostus lactone on selective hydrogenation gives a dihydro derivative which is under investigation.

10·3 *Compounds related to selinane, elemane and p-menthane :* (B-8·16/67)

Compounds related to selinane and elemane are widely distributed in nature and some of them such as santonin are of medicinal value.

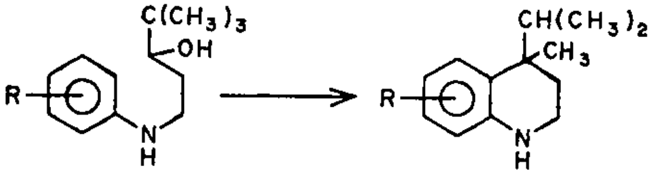
Carissone, dihydroeudesmol and α-eudesmol have been synthesized starting from santonin.

10·4 *Studies in heterocyclic chemistry :* (B-8·7/65)

10·4·1 *Studies in hydride transfer :* To extend the work on the stereochemistry of hydride transfer in linear heterocyclic systems, a number of 2,3-disubstituted quinolines were synthesized. It was found that 2, 3-dimethyl-2, 3-diphenyl, 2-phenyl-3-methyl quinolinium methiodides on reduction with complex metal hydrides give a mixture of Δ^2– and Δ^3– hydro derivatives. However in the case of 6-methoxy-N-methyl-1, 2, 3, 4-tetrahydroacridium iodide tri-*t*-butoxylithium aluminium hydride gives 6-methoxy-N-methyl-1, 2, 3, 4, 9, 10-hexahydroacridine exclusively. This compound on acid catalyzed disproportionation gave *trans* fused octahydroacridine derivative in larger proportion than the *cis* fused octahydroacridine derivative. In view of the nonselectivity of the reductions even with a variety of reducing agent, this work is temporarily suspended.

The stereoselectivity for the *cis* product in the acid catalyzed disproportionation of 3, 4-disubstituted 1, 2-dihydroquinolines and 1, 2-dihydrothiachromans was thought to have originated from the difference in the stability of carbonium ions at C_4 and C_3 positions. To test this hypothesis, the preparation of acetates and tosylates of N-methyl-1,2,3,4-tetrahydroquinoline-4-ol, 1,2,3,4-tetrahydrothiocroman-4-ol and 1,2,3,4-tetrahydro-1-naphthol and that of N-methyl-1,2,3,4-tetrahydroquinoline-3-ol, 1,2,3,4-tetrahydrothiochroman-3-ol and 1,2,3,4-tetrahydro-2-naphthol was attempted. The solvolysis experiments were abandoned in view of the difficulties in product analysis. However, attempts are underway to find out the comparative stabilities of the carbonium ions in question under electron impact.

10·4·2 *Tetrahydroquinolines by carbonium ion rearrangements :* The mechanism of cyclodehydration of various 1-phenylamino-4,4-dimethylpentane-3-ol (I) giving 4-isopropyl-4-methyl-1,2,3,4-tetrahydroquinoline derivatives (II) has been elucidated.

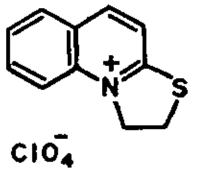


I

II

10·5 *Synthesis of compounds with potential biological activity:* (B-8·31/68)

Various derivatives of a new class of potential psychotropic reagent viz., phenothiaphosphine have been prepared involving a new versatile route. Some of these have been sent for biological testing. Attempts are underway to synthesize phenoazaphosphine and phenothiasilane derivatives which may possess interesting biological activity. A number of N-oxides of 2,3-dihydrofuro (3,2-c) quinolines have been prepared and will be sent for testing soon. Similarly 2,3-dihydro-4-methyl(3,2-c) quinolines, a new series of furoquinolines, have been prepared by cyclodehydration of 3-(1'-methyl-1'-arylamino-methylene) tetrahydrofuran-2-one. The N-oxides and methiodides of the latter compounds were also prepared. The synthesis of the interesting heterocyclic compound; dihydrothiazoloquinolium perchlorate (I) has been achieved starting from quinoline-N-oxide and ethyl mercaptoacetate.



I

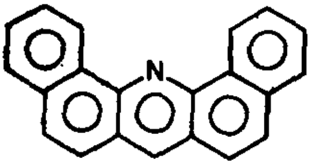
10·6 *Nitrogen heterocyclics :* (B-8·50/69)

The rearrangement observed during the cyclodehydration reactions of *cis*-2-arylaminomethylenecyclohexanones leading to 1,2,3,4-tetrahydroacridines instead of 1,2,3,4-tetrahydrophenanthridines has been studied further. The tautomeric behaviour and the site of protonation of *cis*-2-arylaminomethylenecyclohexanone was studied on the basis of IR and NMR spectroscopy.

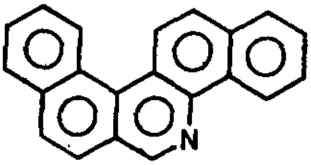
The cyclodehydration reaction mentioned above has been extended for the synthesis of some novel tetra and pentacyclic mono (II a-d) and diaza (III a, b) compounds and some 1, 2, 3, 4-tetrahydroacridine derivatives which were hitherto inaccessible by conventional methods. Other new systems which were synthesized using this general sysnthesis include both the linear (a) and angular (b) analogs of cyclopenta (IV) and cycloheptanoquinolines (V).

A few derivatives of heterocyclic fulvenes (VI, a-c; VII a-c.), a new class of non-alternant 14-electron system have been synthesized. The general method developed for these preparations is being extended for non-alternant non-benzenoid systems containing 16 electrons.

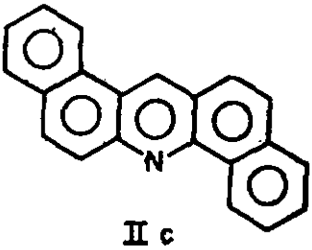
A new and versatile method for the synthesis of N-phenylazetidine and N-phenylaziridine has been developed.



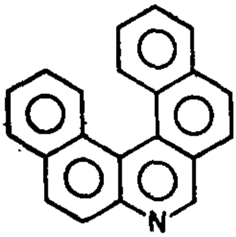
II a



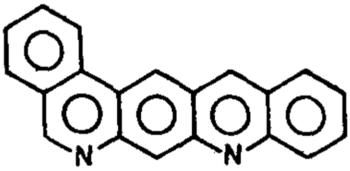
II b



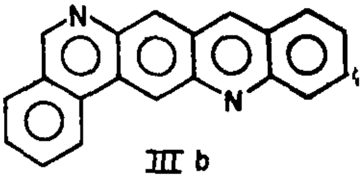
II c



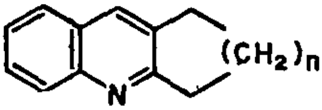
II d



III a

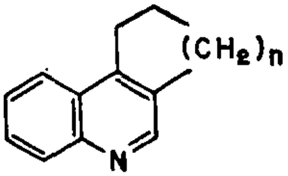


III b



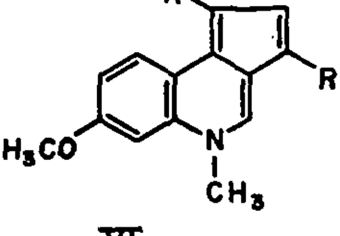
IV a ; n=1

V a ; n=3

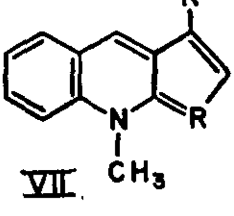


IV b ; n=1

V b ; n=3

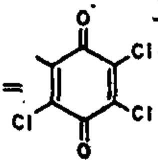


VI

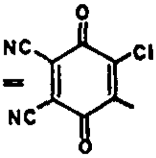


VII

a ; R =



b ; R =



c ; R=SC_6H_5

10·7 *Antifertility drugs:* (AB-25/66)

Yield of the Oppenauer oxidation of the key intermediate 4-hydroxy-8-methoxy-6-N-methyl 1, 2, 3, 4, 4a, 5, 6, 10b-octahydrophenanthridine leading to 8-methoxy-6-N-methyl-4-oxo-1, 2, 3, 4, 4a, 5, 6, 10b–octhydrophenanthridine has now been improved through a two step procedure. The conformational aspects of the reactions involved in this synthesis have now been worked out.

10·8 *Flavonoids:* (B-8·9/58)

Eupatilin, eupatorin and eupafolin, isolated by Kupchan from a plant with cytotoxic properties, were synthesized.

Earlier, it has been shown that 7-hydroxy- or methoxy-flavones on treatment with $POCl_3$ gave 7-chloroflavone. The displacement of a hydroxyl or methoxyl group in the 7-position in flavones can also be effected by refluxing with thionyl chloride in benzene. The action of thionyl chloride and sulphuryl chloride on hydroxy- and methoxy-flavones has been studied.

10·9 *Naturally occurring anthraquinone pigments:* (B-8·10/64)

Work is being continued on a few fundamental and applied aspects of utilizing lac dye. The possibilities of preparing a few useful pigments from crude lac dye are being investigated.

An attempt has been made to synthesize laccaic acid B derivative through *C*-phenylation of the anthraquinone moiety. Thus *bis*-sulphimide of 1, 4-diamino-6-chloroanthraquinone on arylation with *p*-methoxyphenylethanol methyl ether in presence of sulphuric acid and hydrogen peroxide gave mainly the diaryl derivative. However, using aluminium chloride as the condensing agent in the arylation reaction, it was found to give mostly the monoaryl product. Further work in this direction is in progress.

Two structures were suggested by Imere for the pigment isolated from the leaves of *Digitalis viridiflora* on the available spectral data. Both the compounds (1, 6-dihydroxy-3-methyl- and 1,7-dihydroxy-3-methylanthraquinone) were synthesized, and the properties of the latter are in agreement with those of the natural product.

10·10 *Synthetic dyes:* (B-8·8/62)

10·10·1 *The Marschalk reaction:* The Marschalk reaction, which consists in the *C*-alkylation of hydroxy- and amino-anthraquinones by treatment with aqueous sodium dithionite, sodium hydroxide and an aldehyde, was the subject of a few recent patents on disperse dyes. The mechanism of this reaction has now been elucidated by following the progress of the reaction using

NMR spectroscopy. Many compounds have been synthesized employing different aromatic aldehydes, and their dyeing properties are being examined.

10·10·2 *Polycyclic quinones :* With a view to preparing derivatives of polycyclic quinones possessing the requisite volatility for mass spectra and solubility for NMR spectra, the reductive methylation products of some commercial vat dyes were prepared, but proved to be unsatisfactory. Other derivatives are under examination.

Reductive alkylation of anthraquinone gave a product identified as *C*-allyloxanthrone. Treatment of 2-aminoanthraquinone with KOH in DMSO under certain conditions yielded an isomer of indanthrone, as indicated by the NMR and mass spectra of the reductive methylation product, and a second blue product, the structure is being investigated.

10·10·3 *2-Arylanthraquinones :* Arylation of alizarin Saphirol B with phenols or anisole according to the old IG patents in presence of sulphuric acid and boric acid is known to give the 2-aryl derivative with the displace ment of a sulphonic acid group. This product on treatment with alkaline sodium dithionite gave the 1, 5-diamino-3-aryl-anthrarufin which is a valuable brilliant blue dye for polyester fibre. Recent work from the laboratory in the arylation of hydroxyanthraquinones has resulted in the revision of the structure suggested for the arylation product obtained by the IG process. A number of arylated hydroxyanthraquinones have been synthesized with a view to prepare new disperse dyes.

10·10·4 *Synthesis of S-triazole (4, 3-a) - 1, 3, 5-triazines :* Dreivatives of this ring system were prepared earlier from *S*-triazoles and aliphatic or other precursors or from a hydrazino-1, 3, 5-triazine. An improved method of preparation from the latter type of intermediate has been developed. Their use as intermediates for dyes and chemotherapeutic agents is being investigated.

10·11 *Functionalization of saturated aliphatic and alicyclic compounds:* (B-8·46/69)

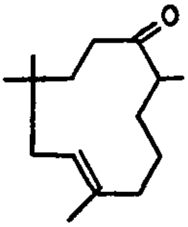
The functionalization of saturated hydrocarbons by photolysis was undertaken with a view to obtain some useful products. The general procedure involves photolysis of hydrocarbons in the presence of peracid using a suitable solvent. The study of the two hydrocarbons i.e. *p*-menthane and methylf cyclohexane is in progress.

p-Menthane: The reaction product obtained seems to be a mixutre o-isomeric dihydroterpineols. One of them was isolated in the pure form by preparative GLC and its characterization is underway. The product distribution as a function of time was carried out and it revealed that the product ratio remained almost the same throughout the reaction period.

Methylcyclohexane : The reaction product obtained was found to be a mixture of four components. The major component (obtained in about 50% yields) was isolated in the pure form and it was found to be 1, 1-methylcyclohexanol. The separation and characterization of other components is in progress.

10·12 *Photochemistry of organic compounds :* (B-8·47/69)

The photoradiation of *trans*-tetrahydrozerumbone (I), a medium ring, non-conjugated ethylenic ketone was studied and the major products of the reaction were isolated and their structures determined on the basis of spectral and chemical data. Besides unchanged starting material and its *cis*-isomer, an oxetane (II) (major component) and two alcohols were also isolated.



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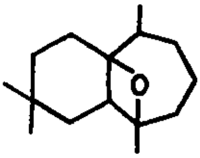


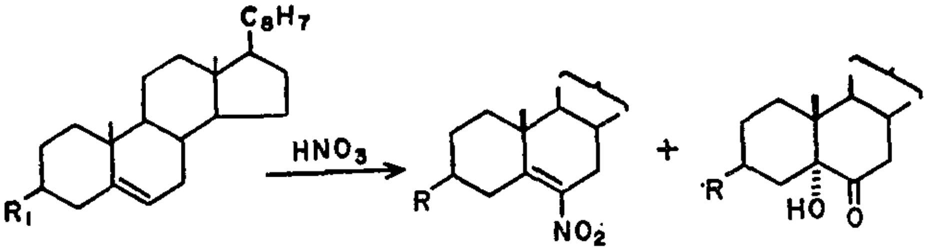
II

10·13 *Prostaglandins :* (B-7·12/70)

Prostaglandins have been used in medicine to induce abortions, to regulate menstruation and fertility, lower blood pressure etc. Work has been started with a view to synthesize this medically important product from simple fatty acids.

10·14 *A novel reaction of nitric acid with steriods :* (B-8·55/70)

Aromatic compounds are nitrated with nitric acid. Besides it is known since the last eighty years, that unsaturated steroids on treatment with nitric acid under very mild conditions, nitrate the double bond. This method has been used by several authors to prepare a nitro steroid. It has now been found that under these conditions, an α-ketol is also produced, which sometimes is the principal reaction product. Hence the main products of this reaction on the unsaturated steroid (I) are now characterized as (II) and (III).



R = H or Cl or OH or OAc or OCH_3

(I) (II) (III)

The mechanism of formation of these products has also been elucidated.

11. PHYSICAL ORGANIC CHEMISTRY

11·1 *Studies on conjugated systems :* (B-5·2/62)

11·1·1 *Donor-acceptor interaction :* (a) *Proton chemical shifts in o-dinitrobenzene derivatives:* Analysis of the NMR spectra of a series of eight substituted 1, 2-dinitro benzenes has been completed using LAOCN-3. In the variations of chemical shifts observed, this system is appreciably different from the structurally analogous phthalic esters studied earlier. While the 6-proton chemical shifts displayed the same variation with donor strength as in the previous system, the 3-proton shifts did not. For the latter shifts, the derivatives seem to fall into two groups. Only the normal shifts expected from substituent effects are seen in the case of the halogen derivatives. For the others, the additional upfield shift resulting from electronic interactions in the system seems to be obtaining. The precise significance of this difference is not yet clear.

(b) *4-Substituted phthalic anhydride :* Proton chemical shifts in phthalic esters were earlier rationalized in terms of conformational changes of the substituent groups. In order to check the correctness of this interpretation parallel series of phthalic anhydrides have been studied. The approximate chemical shifts that have been obtained have given positive indication in this regard.

(c) *Polarographic reduction of o-nitrobenzoic esters :* Polarographic reduction of two series of derivatives (4- and 5-substituted) of 2-nitrobenzoic esters has been studied in an effort to get supplementary evidence on interactions between donor and acceptor groups.

The half-way potentials for a series of 5-substituted compounds showed a regular variation with donor strength, reduction becoming more difficult when donor strength increases. In the series of 4-substituted derivatives studies some abnormality has been seen for the methoxy derivative. However, a trend as seen for the previous series is found. The results suggest that when the nitro group is rotated out of the aromatic plane, its reduction at the mercury electrode becomes more difficult. The relative donor strengths for the two alkyl derivatives is in the order, *t*-Bu >Me in both series. The measured ease of reduction is apparently determined by both inductive and mesomeric effects of substituents.

11·1·2 *NMR spectra of condensed thiophenes:* Two views have been expressed on the nature of bonding of sulphur in thiophene and its derivatives. One view considers that sulphur 3d orbitals are involved and the other excludes them. Proton chemical shifts of a series of condensed thiophenes have been studied to see if any useful indication can be obtained in this regard.

Effects of all possible factors that can influence chemical shifts have been taken into account and it has been concluded that for a proper understanding of the data, the electron donor action of sulphur and its effect on π-electron densities at the aromatic carbon atoms must be considered. This conclusion favours neglect of d-orbitals in the description of sulphur bonding in these compounds.

11·2 *Structural and stereochemical studies:* (B-8·23/68)

Ascorbic acid and its derivatives: As part of a programme on the investigation of biologically important molecules, extensive studies on ascorbic acid and its derivatives have been undertaken since it was felt that the properties of these compounds are poorly understood. Almost all the derivatives reported in connection with the structural work on ascorbic acid have been prepared and their NMR, IR and UV spectra recorded. The significance of the wealth of information thus accumulated is now being estimated.

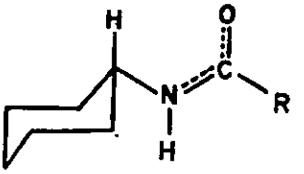
11·3 *Electronic spectra and electronic structure:* (B-5·9/68)

Considerable progress has been made in the study of the electronic structures of ketene, acyl cation, acetic anhydride and cations derived from it. The molecular orbital calculations that have been done employ the CNDO approximation.

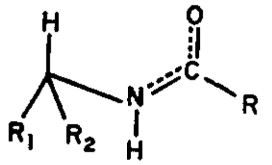
11·4 *Conformational studies:* (B-8·45/69)

It is well known that the conformations adapted by peptide chains in enzymes and other systems have a large part to play in their reactivities. But in these systems intramolecular hydrogen bonds assist the formation of the particular conformation found. It would therefore be of fundamental interest to find whether the basic unit in them, viz., the corresponding simple amide carbonyl group, undisturbed by hydrogen bonding has a preferred conformation.

Secondary amide groups were therefore introduced at various positions in a rigid system as the steroid skeleton and the conformation of the carbonyl group determined by NMR spectroscopy. Later, secondary amides were introduced in flexible simple cyclohexane systems and in long chain hydrocarbons. All of them were found to have a preferred conformation in which the carbonyl group nearly eclipses the secondary hydrogen atom concerned, as shown below (A and B).



(A)



(B)

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

11·5·1 *Bond formation under electron impact:* It is necessary to understand the factors that lead to bond formation induced by electron impact for the successful interpretation of the mass spectra. In continuation of pioneering work in this field many tailor made systems have been examined. A systematic study has revealed some of the important factors which induce bond formation in the vapour phase.

11·5·2 *Free energy relationships in mass spectral fragmentation processes:* In the unimolecular ion decomposition reactions operating in some *p*-substituted benzaldehyde phenyl hydrazones, *m*- and *p*-substituted acetanilides and *m*- and *p*-substituted, *cis*-2-aryl aminoethylene cyclohexanones, ion abundances of a few major fragments were found to correlate with Hammett ' σ ' values. The various factors which determine substituent effects in the gas phase ion descomposition reactions were determined. The significance of Zm/Zp values for simple cleavage and rearrangement processes for *m*- and *p*-substituted compounds was illustrated.

.11·5·3 *Photochemical, pyrolytic and electron impact processes; similarities and differences:* Work was started on a systematic study of the behaviour of some isothiazoles under electron impact. The photolytic and pyrolytic behaviour of these compounds will be examined for comparison. The retro Diel's Alder reaction induced by electron impact was examined carefully to find out the application of Woodward-Hoffmann molecular orbital symmetry rules for ring opening under electron impact.

11·5·4 *Studies on the relative stabilities of carbonium ions in the gas phase:* Mass spectrometry is a useful technique to study the properties of gaseous ions. Very little work has been reported on the use of this technique for the study of stabilities of gaseous carbonium ions. The mass spectra of ∝- and β-tetralols, 3- and 4-thiochromanols and 3-and 4-tetra hydroquinolinols have been examined in order to compare the relative stabilities of carbonium ions generated at C_3 and C_4 positions.

11·5·5 *Characterization of organo-phosphorus compounds:* A few ∝-hydroxy phosphonates and alkyl ethers of *p*-quinol phosphate esters were analysed mass spectrometrically. The major fragmentation reactions operating in these systems were established by deuteration, high resolution and metastable defocussing techniques.

11·5·6 *Biochemical applications of mass spectrometry:* Work has been initiated on the applications of mass spectrometry in biochemistry. Preliminary work on the estimation of chlorinated insecticidal residues on wheat has been completed. Estimation of phosphorus esters has also been standardized.

11·5·7 *Metastable defocussing technique:* Metastable defocussing technique is a very essential technique to identify the parent and daughter ions. The necessary modifications required to operate the instrument in metastable defocussing mode were completed. The technique has been standardized and constantly used in research work.

12. NATIONAL COLLECTION OF INDUSTRIAL MICROORGANISMS: (AB-62/68)

This culture collection consists of non-pathogenic yeasts, bacteria and fungi which are of value in research and industry. Supply of cultures free of charge to research institutions and industries, isolation and identification of cultures for screening programmes in the Laboratory and research on the preservation of cultures are undertaken.

762 cultures were sent to various industries and research organizations. 180 cultures, which were obtained from National Collection of Industrial Bacteria, Aberdeen, Scotland and National Collection of Yeast Cultures, London, as free gifts, were added to the collection. Routine maintenance, subculturing and biochemical tests on the cultures were carried out.

13 compounds from the Organic Chemistry (Natural Products) Division of this Laboratorywere screened for bactericidal and bacteriostatic activity. Work on the preservation of cultures under paraffin oil was continued.

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

This long range project has as its objectives: the study of growth and differentiation of rice, wheat, maize and jowar cultures, which were isolated for the first time in this Laboratory; the metabolism of normal and tumour cells and growth of single cells of plants.

Studies on the nutrition and the metabolism of the four cereal cultures were continued. The uptake of sucrose, amino nitrogen, iron and phsophorus by these cultures in shake flasks was determined. The absolute requirements for amino acids and vitamins for these cultures were studied by repeated subculure on media deficient in individual growth factors. Vitamin B_6 was indispensable for the growth of wheat. Work on other growth factors is in progress. Low concentrations (0·001 to 0·01%) of zeatin showed stimulation of growth of these cultures in shake flasks. Abscisic acid showed a selective inhibition of maize roots with relatively little effect on callus cultures.

Studies on differentiation and organ formation were continued. Whole plant formation was observed in the case of wheat, but only a small percentage of callus cultures formed plants. Work on obtaining whole plants from primary explants and cell lines both of diploid cereal cultures and of haploid callus from anthers of maize, wheat and sorghum was initiated.

Since the growth of single cells of plants in general is very poor, a long term project on defining conditions for cloning plant cells is in progress. 50% efficiency of cloning in the case of apple tissue was obtained. Modifications of the nurse tissue technique are also being studied.

Most of the equipment, chemicals and facilities for beginning work on animal cell cultures have been obtained. Work on the tissue culture rooms is expected to be completed by June 1971.

14. ENZYME

This is a long term project on the isolation, chemistry, regulatory properties and biochemical role of enzymes.

14·1 *Hexokinase :* (B-12·1/63)

The particulate hexokinase of ox heart was solubilized and obtained in highly purified form. It was found to have very little mobility on acrylamide gel at pH 8·4, whereas two isoenzymes present in the soluble fraction of heart muscle were found to have markedly different mobilities. The Ki for glucose-6-phosphate was determined at different Pi and ATP concentrations. The inhibition by ATP was found to be noncompetitive with respect to ADP whereas inhibition by 5-thio-D-glucose was competitive with respect to mannose. The Ki for the latter was 1·4 mM. Several hormones were tested for their action on hexokinase activity directly or in the presence of glucose-6-phosphate and/or Pi, but were found to have no effect.

14·2 *Phytase :* (B-12·2/64)

A bacterial phytase has been obtained in homogeneous form which specifically hydrolyzes only inositol hexaphosphates. The K_m and V_{max} at different pH values were determined. The enzyme was unstable in the absence of calcium due to traces of proteolytic enzymes, but the latter could be selectively inactivated by treatment with diisopropylfluorophosphate. Preliminary work showed that on removal of Ca^{++} with EDTA the enzyme was irreversibly aggregated. Further work on the molecular weight of the enzyme under different conditions is in progress. 60 to 70% of the total phosphorus of the phytase was rapidly hydrolyzed and further hydrolysis upto 90% took place much more slowly whereas the residual phosphorus was not hydrolyzable. Inositol-2-phosphate was also not hydrolyzed even with large quantities of enzyme.

14·3 *DPNase :* (B-12.7/68)

The isonicotinic acid hydrazide-sensitive DPNase of ox brain was purified about 400-fold. Studies on the kinetics of the enzyme with different substrates and at different pH values and on the effect of inhibitors are being continued.

14·4 *Acylphosphatase :* (B-12·7/68)

Acylphosphate hydrolyzing enzymes of plant tissues have not been studied hitherto. There was considerable variation in the results on the purification of the enzyme from different lots of *Vigna catjang*. A method for obtaining reproducible results for the purification of the enzyme from this source was finally standardized. The purified enzyme had no activity with carbamyl phosphate, ATP or glucose-6-phosphate and was specific for acetyl phosphate. The enzyme was inactivated by bisulphite and on removal of bisulphite only half the original activity was recovered. The enzyme was irreversibly inhibited by Hg^{++}. Iodoacetate and PCMB inhibited the enzyme but sulphydryl compounds had no effect on enzyme activity. The purified enzyme did not show glyceraldehyde-3-phosphate dehydrogenase activity. The isolation of the other phosphatases which also act on acylphosphatase is being studied.

14·5 *Enzymes and the metabolism of organic acids:* (B-12·8/68).

14·5·1 *Bacterial degradation of citramalate :* The three enzymes concerned with citramalate metabolism (succinate activating enzyme, succinate citramalate CoA transferase and citramalyl cleaving enzyme) were separated from each other. The succinate activating enzyme was obtained in highly purified form, and its properties, specificity and kinetics were studied. The transferase was relatively labile. Both the activating enzyme and the transferase showed activity with itaconate though at a lower rate than with succinate. Experiments on the reversal of the reaction and the identification of the optical isomer obtained by synthesis are in progress.

14·5·2 *D-Malate dehydrogenase :* The method for the purification of the enzyme is being stndardized. The enzyme requires at least 0·01 M K^+ for its activity and stability. The characterization of the pure enzyme by acrylamide gel electrophoresis and ultracentrifuge studies is in progress. The purified enzyme is labile.

14·6 *Metabolism of nitrate by A. fischeri :* (B-12·6/65)

Studies with isolated enzymes involved in nitrate metabolism of *A.–fischeri* were continued. Further investigations with pure nitrite reductase show that it contains 18 mumoles of heme C per mg. of protein and 0·102% iron. The molecular weights determined from these values were found to be one-half the molecular weight determined by ultracentrifugal analysis indicating that 2 molecules of heme or two atoms of iron are present per molecule of enzyme.

Studies on the kinetics of inactivation of nitrite reductase with protein denaturants were continued. The substrates, nitrite and hydroxylamine were found to protect nitrite reductase against urea inactivation.

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

Studies on the structure-function relationships of the enzyme from *Aerobacter aerogenes* were continued. The role of metal in activation of the enzyme was studied using radioactive Mn^{++} as probe. The unique binding of metal was established by equilibrium dialysis and by gel permeation techniques. The role of the metal in stabilizing the quaternary structure of the enzyme under dissociating conditions was also established.

Studies are in progress on the primary sequence around the active site covalently labelled by C-14 tagged inhibitor.

A pure enzyme has been isolated from a different bacterial source with properties markedly different from the *A.aerogenes* engyme. The preparation is being studied for its usefulness as an analytical tool in routine citrate assay of biological samples.

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

The problem of toxicity due to organophosphorus insecticide residues is closely related to the inhibition of several carboxyl esterases in the animal system. Liver, kidney and lung are particularly rich in such enzymes whose normal physiological function is not known. On treatment with diisopropyl phosphorofluoridate (DFP) both *in vivo* and *in vitro*, it has been found that the Na^+ and K^+ contents of mouse liver tissue are significantly altered. Acetylcholine and eserine in combination at low concentrations of 10^{-6} M each also effect similar changes in the Na^+ and K^+ contents. The (Na^+-K^+)-dependent ATPase is not present in liver tissue and the Mg^{2++} dependent ATPase is unaffected by 10^{-5} M DFP.

14·9 *Screening of microorganisms for the preparation of industrially important enzymes :* (AB-67/69)

Many of the industrially useful enzymes like amylase, protease, cellulase etc., needed for the pharmaceutical and other industries are partly or wholly imported. The object of this long range project is to screen a large number of organisms for their potential enzyme producing activity as well as to produce mutants capable of exhibiting certain special properties like acid resistance etc.

Cellulase

Studies on the isolation and screening of microorganisms for obtaining high cellulase producing strains useful in industrial utilization of cellulosic wastes were continued.

Out of new isolates obtained during this year, 12 showed promising cellulase activity.

Preliminary studies were carried out on the effect of incorporating different nitrogen and carbon sources in the growth medium used for *Trichoderma* and *Aspergillus* on enzyme production. Ammonium sulfate, wheat bran extract and Tween-80 incorporation enhance cellulase activity. The optimum pH for enzyme production was 5·0 - 5·5. Further studies in this regard with other isolates are in progress.

Mutation studies with an *Aspergillus* culture have been initiated and a few mutants obtained in these studies are being tested for their performance.

Amylase

The group of black *Aspergilli* in the NCIM had been screened under a certain set of conditions of growth for their ability to produce extracellular amylase and the enzyme activity had been followed by two methods. During the year under report, the existing strains (about 25) of *Aspergillus oryzae* have been investigated for their capacity to produce amylase and the methods employed have been similar to the ones used with *A. niger*. Besides these cultures, nine fungi isolates have been made and these have also been tested. Three cultures of the *oryzae* group and two of the isolates show promise as potential amylase producers. The strains of the *A. niger* group, those of the *oryzae* group and the isolates (which had shown promise as good extracellular amylase producers) were grown under suitable conditions and the crude enzyme in the fermented liquor was tested for their stability at pH 2·5 for 30 minutes and a temperature of 37°. An analysis of the activity of these cultures showed that only a few strains (about two or three) excreted amylase which had at least about 40% stability under the test conditions. The other strains lost completely their activity. Studies had also been carried out by the use of stabilizers like sodium chloride, calcium chloride etc., to render the enzymes more resistant to the acidic conditions under investigation. Here again there is good promise of stabilizing the enzyme under certain set of conditions. These are in the process of further experimentation to establish firmly this property.

15. STUDIES IN POLYMERS

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

Further work on the polymerization of methyl methacrylate with Cr (AcAc)- $AlEt_3$ at ratio 12 of Al/Cr was carried out. It was found that in presence of triethylamine and hydroquinone, yield of the polymer was unchanged but its structure changed from stereoblock to heteroblock. Heteroblock structure of the polymer was also obtained by using aluminium alkyl alone with hydroquinone or triethylamine. From further experimental data, it was concluded that excess of $AlEt_3$ in association with complex of Al/Cr ratio of 3 is responsible for the polymerization of methylmethacrylate by anionic mechanism.

The use of aluminium tri-isobutyl in place of aluminium triethyl under similar conditions gave higher yield of the polymer. The rate of polymerization was found to be directly proportional to the catalyst concentration while it was independent of monomer concentration, indicating the effect of gel formation in the reaction system. In general, it appears that the mechanism of polymerization may differ with the change of the alkyl. Further work is in progress.

Copolymerization

In order to obtain higher yield of styrene-acrylonitrile copolymer with $VOCl_3$-$AlEt_3$ catalyst system, the effect of the order of mixing the reagents was studied. It helped to improve the yield of the copolymer considerably. It was also noted that at higher concentration of acrylonitrile, reaction mixture was violet and at low concentration it was brown in colour. Change of colour from brown to violet indicates reduction state of V^4 to V^3. It was further found the use of VCl_4-Aluminium triethyl, VCl_4-Aluminium tri-isobutyl, $VOCl_3$-Aluminium tri-isobutyl gave considerably higher yield of the copolymer. The copolymers are also alternate in structure but due to their linearity, they melt around 140°.

15·2 *Polymer characterization* : (B-14·14/69)

Thermodynamic aspects : Thermodynamic *data* on monomers and polymers are valuable for understanding, predicting and controlling the course of industrial polymerizations and properties of polymers. Such data in this relatively new area of chemistry are sparse. However, it is virtually impossible to obtain such complete experimental data on the vast array of monomers, polymers and compounds related to plastics industry. A theoretical research tool viz., a new bond-energy scheme for predicting thermodynamic properties within a precision of 0·5 kcal./mole is being developed. Work on heats of formation of alkanes and alpha-olefin polymers has been published.

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

The ultrasonic degradation of macromolecules has some resemblance to mechanical degradation and the process gives relatively sharp molecular weight distribution within a very short time.

The study of break-down kinetics of Neoprene AD was continued. In course of this work, however, molecular parameters such as second virial coefficient, radius of gyration, root mean square end-to-end distance of chains, Flory's universal constant etc., in chloroform solution were determined. It was found that in Neoprene AD there was a wide range of distribution of molecular weight ($0.52—33{\cdot}86\times10^5$). The root mean square end-to-end distance $[<\overline{\gamma^2}>_\varepsilon]^{1/2}$ of coiled molecules vary regularly in the same direction as the weight average molecular wight.

16. CHEMICAL ENGINEERING STUDIES

16·1 *Utilization of surplus petrochemicals :* (AB-84/70)

The project has been undertaken to develop a process for the preparation of ethylbenzene from benzene and ethyl alcohol, or ethylene, by use of molecular sieve catalyst being developed in the Physical Chemistry group.

An all-glass laboratory apparatus and suitable inert packings, tested for non-activity under experimental conditions, were used for investigation experiments. Catalyst activation was done using oxygen at 400°, and the product mixtures were analysed by VPC. An unsubstituted X-type catalyst was first tried using various feed compositions, rate and temperatures up to 350°. The base catalyst did not show any significant activity. The rare earth promoted catalyst X-RE-l was tested in a similar manner, whereby slight formation of ethylbenzene was noticed. The testing of the second promoted catalyst X-RE-2 is in progress. This and the subsequent catalyst will be tested at two temperatures : 180° and 210°; at two feed compositions : 1:3 and 1:5 alcohol benzene molar ratios; and at one feed rate. A laboratory ethylene generator is being set up to study this catalyst reaction, also with ethylene and under pressure if possible.

16·2 *Fluidization :* (B-14·5/68)

The 18" fluidization column, set up for studying the uniformity of fluidization was found to operate satisfactorily. Work on the instrumentation of the column and preparation of tapered inserts was continued.

16·3 *Mass transfer :* (B-14·6/68)

Investigations on flooding and hold up in a pulsed liquid extraction column were completed and suitable mathematical models developed for predicting flooding and hold up both in pulsed and unpulsed columns.

16·4 *Reaction models and reactor design :* (B-14·8/68)

16·4·1 *Experimental reactors :* The mixing characteristics of a pulsed fluidized bed reactor were studied and an assembly was set up to determine the residence time distribution (RTD) in this reactor. Two types of stirred reactors were fabricated and RTD studies were carried out on these reactors also. It was found that they operate as fully mixed reactors. Mass transfer data was collected by evaporation from naphthalene balls, and correlations were developed to predict the mass transfer coefficient under different conditions of stirring and gas flow rate. A reactor has also been set up for determining the kinetics of a reaction exclusively from the temperature profile in an adiabatic system.

16·4·2 *Studies in gas-liquid-solid reactions :* The heterogeneous reaction, hydrogenation of glucose on suspended Raney nickel catalyst, was used as an ideal reaction for studying this system. It was found that there is a definite transition from diffusion to chemical control around 100°. In the kinetic regime, various heterogeneous models were tested based on which 3 likely candidates have been identified. These three models are now being subjected to various statistical discriminatory tests to arrive at the final model.

16·4·3 *Gas-liquid reactions :* The system, hydrogen chloride plus ethylene to give ethyl chloride in a medium of nitrobenzene containing aluminium chloride as catalyst, was chosen because of practical importance of ethyl chloride used in the production of tetraethyl lead. Solubilities and diffusivities of ethylene and hydrogen chloride in nitrobenzene as well as ethylene dichloride were separately determined at different temperatures. Study of absorption of ethylene with chemical reaction in nitrobenzene containing hydrogen chloride and dissolved catalyst ($AlCl_3$) was carried out in a surface stirred vesel at different stirring speeds, partial pressures of ethylene, catalyst concentrations, and hydrogen chloride concentrations. An analysis of this data based on surface renewal model is in progress.

16·4·4 *Gas-solid reactions :* Mass transfer model proposed for the oxidation of zinc sulphide sphere has been modified for case of cylindrical pellets. Experimental work has been carried out on the oxidation of zinc sulphide using right circular cylindrical pellets ($L=D$) and cylindrical pellets with $L \neq D$. In kinetic range, the Levenspiel model still holds good and the modified mass transfer model fits the data in the diffusional regime of control. Work on oxidation of cadmium sulphide was not continued because of the complexity of the reaction mechanism. Work is being extended to the oxidation of sphalerite ore from Rajasthan and oxidation of ferrous sulphide.

16·4·5 *Solid catalysed vapour phase reactions :* The kinetics of the isomerization of *n*-butene was being studied on a catalyst selected by the method of group screening. The objective of this work is to assess the various types of model building and discrimination techniques proposed and also to determine the surface area during catalysis. Both power law and Hougen-Watson models have been considered.

The kinetics of the vapour phase esterification of acetic acid with a series of alcohols (C_2 to C_{10}) on silica gel are being studied. Work on one alcohol has been completed. Simultaneously the kinetics of the vapour phase esterification of ethyl alcohol with different acids (C_2 to C_{10}) are also being studied. The object of this work is to establish generalized models for esterificatio-n reactions and to propose methods for predicting the rate and adsorption con stants from physico-chemical data.

16·4·6 *Models for catalyst fouling :* A model has been developed for predicting the performance of a fouling catalyst in fixed, fluidized and moving bed reactors for a consecutive reaction system. This model is now being examined experimentally by using the chlorination of tetrachloroethane on active carbon as a convenient system.

16·4·7 *Catalyst selection :* One of the recent methods used in the selection of catalyst is the so-called group screening technique. This method was successfully employed in screening over 40 catalysts in essentially 17 runs for the isomerization of *n*-butene to isobutene. Fluorinated alumina was found to be the most suitable catalyst. It is proposed to use this technique for several other catalytic systems.

16·5 *Fractional crystallization :* (B-14·14/70)

Continuous fractional crystallization offers certain advantages over conventional methods of separation with regard to energy consumption, size of equipment, number of stages required etc. Though its versatility has been proved beyond doubt no information is available for scale-up etc. Work was started with a 50 mm. dia. glass column with *p*-dichlorobenzene-*o*-dichlorobenzene system. A metallic column was fabricated to obviate the mechanical difficulties presented by the glass column. Work will be continued to study the effect of various parameters such as reflux ratio, column throughput on separation efficiency.

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INFRASTRUCTURE ACTIVITIES

1. DIVISION OF TECHNICAL SERVICES

Research analysis

Proposals giving details regarding the techno-economic aspects, cost estimates, inputs, parties interested in commercial exploitation, terms of release, etc., were prepared. These were put up before the NCL Process Release Committee at their meetings held on 18th August 1970 and 13th March 1971 to obtain their approval for release of these processes to the industry. These included following projects :

phenyl acetic acid, mannitol/sorbitol from cane sugar, 70% sorbitol from dextrose monohydrate, nitrile rubber, fine chemicals project, vitamin B_6, butyloctyl phthalate, glyceryl guaiacolate, carbazole dioxazine violet pigment base. In addition proposals for revision of terms for polyurethane coatings, dimethylaniline, α-terpineol and disperse dyes were also prepared.

Cost evaluation for projects which are suggested in the research programme are undertaken at different stages of development. During the year, cost evaluation was undertaken for the following processes :

cellulose powder, pulp from cotton linters, CMC from groundnut shells, ethyl cellulose, substitute for Separan AP-30, hexachloroethane, ethyl silicate, aluminium chloride from bauxite, quinidine.

A basic note on methodology of undertaking cost/benefit analysis of NCL projects and groups was prepared. This note was discussed at length in all Advisory Panel Meetings held in August 1970. Opinions and suggestions received from the panel members and NCL scientists were submitted to the NCL Executive Council for their advice. Most of the members of the Advisory Panels and Executive Council appreciated the idea and the methodology and suggested NCL to undertake such studies on applied projects in the first instance. Accordingly cost/benefit studies on the following projects were undertaken as a pilot study :

diethyl-*m*-toluamide, silicone and silicone intermediates, polycrystalline silicon, 2-aminopyrimidine, fine chemicals project, ethylenediamine, nitrile rubber, polysulphide rubber, ethanolamines.

It is hoped that in the Research Programme 1972-73, data on cost/benefit will be incorporated on all applied projects.

The priority project of polycrystalline silicon was programmed by PERT and schedules of (i) actual experimental work and (ii) glass and silica fabrication were drawn and followed up.

Work on product encyclopædia of following completed projects is in progress :

simazine and atrazine, butyl titanate, chlorinated methanes, aniline, dimethylaniline, tert-butylcatechol, chlorobenzenes.

Commercial intelligence

Compilation and documentation of techno-economic, market and scientific data relevant to NCL research programme, was regularly carried out from the newspapers, journals and through correspondence.

As follow-up actions of Advisory Panel suggestions technoeconomic data is being collected on the projects mentioned below :

electronic tensile strength tester/stress relaxometer, UV visible spectrophotometer, D. C. polarograph, E. P. R. spectrometer, synthetic gem stones, acid-stable amylase, morpholine, diallyl phthalate, alhydrogel, ethyl silicate, aluminium silicate, silica-alumina cracking catalyst, iron powder from anhydrous ferrous chloride, theophylline, sulphadiazine, quinidine, rare sugars, glyoxal, polymer for oil well drilling, substitute for Separan AP-30.

Industrial liaison

Sponsorment proposals for following projects were prepared :

p-phenetidine, new ingrain dyes, methyl vinyl ether/maleic anhydride polymer, testing methods for ceramic compositions, ethylene urea and dimethylol urea (oxy-urea), *p*-nitroacetophenone, cationic dyes for acrylic fibres, acrylic acid/acrylates from acrylonitrile, propylene oxide from propylene, chlorination of bauxite residue, thermosetting resin for industrial laminates, synthesis of potential pharmacologically active substances, dinonyl phenol, adephenine hydrochloride, chlorinated diphenyls, lauryl sulphate, extraction of sandalwood oil, hydrogenated rosin esters.

Work on first 12 projects has already been sponsored in the laboratory by different parties.

A detailed techno-economic feasibility report on dissolving pulp was prepared and circulated to project engineers and possible entrepreneurs.

2135 enquiries pertaining to NCL projects and general technical enquiries from different individuals, industries, Govt. organisations and starred questions from the Parliament were attended to.

Comments on 166 applications for industrial licences with foreigncollaboration were sent to the CSIR.

2600 visitors from educational institutions, industries and the public were shown round the laboratory during the year.

Entrepreneurs visiting NCL are attended to and information on know-how available at NCL is furnished. During such individual consultancy, new projects which can be sponsored in NCL are often identified.

A press conference was held in August 1970 and a hand-out in English and Marathi describing the achievements of the laboratory was released to the Press. Director, NCL, alongwith his senior colleagues, replied to the Press queries.

Another press conference was held in December 1970, wherein, highlights and recommendations of the seminar on 'Problems of transition from laboratory research to industrial applications', were released to the Press in English and Marathi.

Liaison with CSIR

About 30 NCL processes which had been cleared by the NCL Process Release Committee for release to the industry were referred to CSIR/NRDC for licensing to the interested parties. Non-technical notes including costing were also prepared and circulated to likely users of the technology.

A close liaison was maintained with the CSIR. Every month reports relating to the activities and achievements of NCL were sent for inclusion in the monthly report to the Union Cabinet, CSIR News and Research Utilzation Data.

Popular write-up on 8 NCL processes which have been released to industry were prepared. In addition, abstracts of 4 Ph.D. theses submitted by NCL scientists were also prepared. These were published in CSIR News.

Internal co-ordination

DTS acts as a Secretary to the Action Committee. The Action Committee meets every month and reviews work on the priority projects. The purpose of this Committee is to clear the obstacles in proper execution of priority projects so that they may be completed within the time targets. During 1970-71, 10 NCL projects were on the priority list.

DTS also acts as Convener to the Senior Common Room Meeting wherein senior scientists of the laboratory meet every month and problems regarding planning, execution and progress of work on the laboratory are discussed.

As a part of the internal co-ordination programme, bi-monthly seminars on NCL projects were initiated. These seminars are open to all scientists of the laboratory. This provides a forum for interdisciplinary approach and cross fertilization of ideas.

A close contact with the programme and activities of the laboratory is maintained by associating one member of the DTS to each division.

The division continued to render statistical, photographic and draftsman services to other divisions in the laboratory.

Research management studies

Resource allocation for R and D projects

A study was undertaken from the need for a convenient method to precompute the economical range of expenditure to be incurred on any R and D project to be undertaken by a research institution having no direct participation in the commercialization of the technology it develops. The income aspect has been used to provide an idea of the justifiable expenditure commensurate with the return that the institution hopes to earn on its technology by licensing it to industry for commercial exploitation. A nomogram based on certain essential parameters such as the expected sales turnover, royalty rates, interest rates and life of the technology has been proposed to forecast the respective quantum of investment.

Improving the process efficeincy

In any batch process, a 100% efficiency in the utilization of all equipments and services will not be feasible. This will be possible only if all the processing steps of the batch consume the same length of time and there is no limit to the availability of men and utilities.

A graphical method to maximize the utilization of the equipments and the service units has been suggested.

In collaboration with North Western University, Illinois, U. S. A., data on transfer of technology or projects released by NCL for commercial exploitation was collected.

Literature survey regarding work on personnel policies, resource allocation for R and D projects and patents as instruments of research profitablility was carried out.

An International seminar on 'Problems of transition from laboratory research to industrial application', was held at the National Chemical Laboratory, Poona, from 9th to 14th December 1970 under the joint auspices of UNESCO and the Govt. of India/CSIR. DTS took active part in the seminar. A volume covering the proceedings of the seminar and the papers presented is being brought out shortly.

Reports

(i) *NCL Annual Report 1969-70*

The NCL completed twenty years of service to the Nation in January 1970. In the annual report 1969-70, a review of progress made during the last twenty years was presented. With the help of 9 tables and 11 graphs, and overall cost/benefit analysis of the work of the laboratory during 1950-70 was presented.

(ii) NCL Half-yearly Report (April-September 1970)

(iii) NCL Research Programme (1971-72)

Publications

(i) Adke (Mrs.), S. S., Rajan, J. V. and Subramanian, S. K.
Resource allocation for R and D projects in developing countries.
I.E.E.E. Trans. Engg. Management, EM-18, Feb. 1971.

(ii) Rajan, J. V.
Dissolving pulp industry.
MBI's Indian Industries Annual, 1, 1970.

(iii) Saraf, C. U. and Lele, A. M.
National Chemical Laboratory.
Sampada, 47, April 1971.

(iv) Technology transfer—Summary of views by some R and D establishments and industries in India. Background paper prepared for International seminar on 'Problems of transition from laboratory research to industrial application'.

2. PHYSICO-ANALYTICAL GROUP

This group is engaged in the chemical examination of raw materials, intermediates and finished products related to the various projects in progress in the laboratory. Besides routine testing, involving modern techniques such as ultra violet, visible spectrophotometry, emission spectroscopy, flame photometry, polarography, ion exchange etc., developmental work on new analytical procedures, is also undertaken.

During the period under report, 200 samples from various projects have been tested for quality control and analysis. In addition analytical procedures for the following projects were standardized.

p-Nitrophenol : *p*-nitrophenol and associated impurities of nitro products were reduced at the d.m.e. wherefrom the total nitro compounds were estimated. The organic impurities were separately determined polarographically after isolating them by steam distillation.

p-Aminosalicylic acid : The method is based on the fact that salicylic acid groups coordinate with ferric iron to form intensely red soluble products. Spectrophotometric measurement was conducted at 465 mμ at pH 4 in presence of excess ferric iron. *M*-aminophenol is unreactive under these conditions.

3. MICROANALYTICAL GROUP

Microanalysis of organic and organometallic compounds for various elements, functional groups and other estimations like molecular weight determination, neutralization equivalent etc., are routinely undertaken, in the laboratory for various research groups. Depending upon the internal work load, microanalytical work is also accepted from other research organizations and universities on payment of charges.

During the period, 2230 samples were analysed for various elements (2174) and functional groups (56), of these 185 analyses were carried out for outside parties.

Analysis of industrially important imported organic compositions and auxiliaries available under different trade names were studied for identifying their components with a view to their import substitution. This work is usually undertaken on payment of fees on behalf of interested parties.

During the year four products were identified and reports submitted to parties concerned.

In addition to the above, basic studies in microanalytical chemistry and related subjects are undertaken. Work on the following is in progress: (a) simultaneous estimation of chlorine and bromine in organic compounds; (b) estimation of sulphur in organic compounds containing sulphur and phosphorus; (c) use of silica gel as an adsorbent for moisture in the microdetermination of carbon and hydrogen.

4. ENGINEERING SECTION

Following special installations are routinely operate and maintained : liquid air plant, liquid nitrogen plant, ice plant, cold storage plant, air conditioning plant of about 40 T. capacity, window type air conditioners (60 Nos.), refrigerators and water coolers.

Apart from rendering day to day maintenance and engineering services such as steam, compressed air, vacuum, gas, water and electricity to the laboratory, pilot plants as per the designs supplied by the scientist and special equipments have been fabricated.

The total turnover of job orders executed by this section during the year was over 3,000.

A few of the pilot plant fabrication jobs carried out during the year are mentioned below :

silicon intermediates, aniline, ethylenediamine, *p*-nitrophenol, titanium tetrachloride, vitamin B_6, sulpho-chlorination of polyethelene, equipment for aqueous extraction of medicinal plants and concentration of the extract.

Special equipment facricated

This section also undertakes developmental work on fabrication of equipment and components which save foreign exchange. Following have been fabricated during the year :

(i) expansion coil with all its fixtures for liquid air plant to formulate expansion chamber unit,
(ii) high pressure gland packings of special materials and design,
(iii) 'Parr' type hydrogenators,
(iv) CRAIG type evaporators.

Special jobs conducted

Two sterile rooms for tissue culture laboratory have been constructed and equipped.

5. GLASS BLOWING SECTION

The section undertakes repairs of glass apparatus for research groups in the laboratory. During the year, 2402 repair jobs were completed.

Various types of glass assemblies are fabricated as per the specific drawings furnished by the scientists. 2123 fabrications of glass assemblies were carried out this year.

4986 standard ground glass joints of BM and BF series were fabricated for captive use. .

6. INSRTUMENTATION SECTION

The section is primarily responsible for maintenance and upkeep of electronic, optical and electromechanical instruments such as NMR spectrometer, IR, UV and visible spectrophotometers, X-ray spectrometer, gas chromatographs, colorimeters, servorecorders, electrical furnaces, flame photometers, microbalances, various types of meters, gauges and indicators. The work includes tracing of the faults and rectification to avoid further occurences. Attempts are also made to improve the existing designs and fabricate spare parts for replacement.

Testing of various types of spares particularly useful for the servo controls and spectrometers manufactured in India is carried out regularly. Servomotors, servoamplifiers, fractional H. P. motors, operational amplifiers and integrated circuits were tried for the basic recorder developed in the section, and gratings and optical components were sucessfully used in the spectrophoto meters.

Special equipments fabricated

(i) Heat energy control using solid state circuitry was designed and fabricated using all indigenous descrete components. This S.C.R. energy proportion control occupies less than a quarter of the space occupied by equivalent variac and valve ancestor and will replace them in laboratory equipments such as melting point apparatus and VPC. This developmental work will reduce the overall size of these equipments.

(ii) An input transformer was designed and fabricated for the millivolt recorder developed in the laboratory. Trials show about ten fold increase in sensitivity and reduce bandwidth thus enhancing better performance of the recorder.

(iii) New solid state 'automatic' circuit for electronic flash was devised. The results are promising. Same circuit has been incorporated in the laboratory owned flashguns which previously were of the vibrator convertor type.

(iv) Constant voltage supply of the UNICAM spectrometer was replaced by a solid state constant voltage regulator. Similarly constant voltage supplier was designed and fabricated and tested for replacement of accumulators used in direct reading spectrophotometers and VPC.

(v) A thermostatic bath with 0·1° control was fabricated and is giving satisfactory service.

7. PHYSICAL ORGANIC ANALYSIS

Spectrochemical work

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

Number of samples studied :

NMR	2,866
UV	703
UV - visible	447
IR	5,767
Mass spectra	1,318
BET surface area measurement	13
DTA/TGA	19

VPC/GLC Analysis

4358 samples were analysed.

X-ray patterns

44 X-ray powder patterns were obtained.

8. SERVICES RENDERED TO OUTSIDE PARTIES

Supply of cultures

762 cultures from the National Collection of Industrial Microorganisms (NCIM) were supplied free of charge to various institutions in India and abroad.

Analytical services

During the period a large number of analyses were done for universities, research institutes, Govt. departments, private parties, etc.

The following analyses were carried out :

Microanalysis	185
NMR	70
IR	132
UV	12
UV-visible	37
VPC/GLC	2
Mass spectra	270
BET surface area measurement	10
DTA/TGA	3
X-ray powder patterns	16

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

	Nature of work	*Name of the party*
1.	B-H measurement of ceramic magnet	M/s Tempo Semiconductors, Bombay-57.
2.	Electron micrographs of 3 silica samples	M/s Synthetics & Chemicals Ltd., Bombay-20
3.	One kg. of barium titanate prepared and supplied	M/s Tempo Semiconductors, Bombay-57.
4.	Samples of electrical conducting glass supplied	Instruments Research and Development Establishment, Raipur
5.	Extraction of vanadium and its conversion to ammonium vandate from spent catalyst examined	M/s Gwalior Rayons, Gwalior.
6.	Analysis of diaminostilbene disulphonic acid	M/s Aniline Dyestuffs and Pharmaceuticals Ltd., Bombay-1.
7.	Analysis of Ilmenite	M/s Botanium & Reduced Ltd., Bombay-1.
8.	Analysis of inorganic sample	M/s Sudarshan Chemicals Industries (P) Ltd., Poona-1.

9.	Analysis of inorganic substance	M/s Calico Chemicals & Plastics, Bombay-74.
10.	Analysis of rosin	M/s Johnson & Johnson, Bombay-20.
11.	Analysis of toxaphene	M/s Bharat Pulverising Mills (P) Ltd., Bombay-25.
12.	Analysis of caprolactum (4 samples)	M/s Century Enka Ltd., Poona-26.
13.	Facilities for carrying out experiments	M/s Kirloskar Oil Engines Ltd., Kirkee
14.	Spray drying facility	M/s Sathe Biscuit & Chocolate Co. Ltd., Poona.
15.	A complete unit for aqueous extraction of herbal drugs fabricated	M/s Hamdard (Wakf) Laboratories Ltd., New Delhi.
16.	Supply of liquid nitrogen	(i) Arvi Satellite Communication Project, Dept. of Atomic Energy, P.O. Arvi, Dist. Poona. (ii) Dept. of Animal Husbandry, Maharashtra State, Poona. (iii) University of Poona, Poona. (iv) M/s Bharatiya Agro Industries Foundation, Urulikanchan, Dist. Poona.
17.	*Repair and servicing carried out by the instrumentation group*	
	(a) pH meter and flame photometer	Chief Soil Survey Officer, Govt. of Maharashtra, Poona.
	(b) pH meter and colorimeter	Soil Survey Dept., Govt. of Maharashtra, Padegaon.
	(c) UV spectrophotometer (Perkin Elmer Model-137)	Institute of Armament Technology, Girinagar, Poona-25.

(d)	Spectronic-20 colorimeter	Govt. Science College, Rewa.
(e)	Spectrophotometer	M/s Hindustan Antibiotics Ltd., Pimpri, Poona

18. *Fabrication/repair work carried out in glass blowing unit*

(a)	Three necked flask with accessories, 20 lit. capacity (2 Nos.)	M/s Lona Industries (P) Ltd., Ladivali, Dist. Kolaba.
(b)	Glass apparatus as per sketch (one unit)	Indian Meteorological Dept., Poona-5.
(c)	Condenser and scrubb (one each)	M/s Swastik Laboratory and Industrial Chemicals (P) Ltd., Poona-5.

Total receipts from the anlaytical and other services rendered to outside parties.	Rs. 65,300/-

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APPENDICES

A-I DEMONSTRATIONS

Following processes were demonstrated :

	Process	*Party*
1.	Cadunium sulphide photoconductive cells	M/s Chinoy Electronics, Poona-1.
2.	Catechol	M/s Percynic Chemicals (P) Ltd., Bombay-1.
3.	*m*-Diethylaminophenol (sponsored)	M/s Sahyadri Dyestuffs & Chemicals (P) Ltd., Poona.
4.	Dihydroisojasmone	M/s Sonebon Laboratories, Kottayam-5.
5.	Hexachloroethane	M/s Industrial Oxygen Ltd., Poona-14.
6.	8-Hydroxyquinoline (sponsored)	M/s Alta Laboratories, Khopoli.
7.	Nicotine sulphate	M/s Coromandel Tobacco Bye-products, P. O. Gannavaram, Andhra Pradesh.
8.	*p*-Nitrophenol	M/s Hindustan Organic Chemicals, Rasayani. Licence is being executed.
9.	Peach aldehyde	M/s Sonebon Laboratories, Kottayam-5.
10.	Phthalates (DOP)	M/s India Carbon Ltd., Bombay, through project engineer—M/s R. L. Dalal & Co., Bombay.
11.	tert-Butylcatechol	M/s Percynic Chemicals (P) Ltd., Bombay-1.

A-II PROCESSES LEASED OUT DURING 1970-71

	Process	*Party*	*Remarks*
1.	Butyl titanate	M/s Synthochem, Indore-1.	Non-exclusive. Agreement in progress.
2.	Cadmium sulphide photoconductive cells	M/s Chinoy Electronics, Poona-1.	Non-exclusive.
3.	Catechol	M/s Percynic Chemicals, Bombay-1.	Non-exclusive.
4.	Dihydroisojasmone	M/s Sonebon Laboratories, Kottayam-5.	Non-exclusive.
5.	Hexachloroethane.	M/s Industrial Oxygen (P) Ltd., Poona-14.	Non-exclusive. Agreement in progress.
6.	Nicotine sulphate	M/s Coromandal Tobacco Bye-Products, P. O. Gannavaram, Andhra Pradesh.	Non-exclusive.
7.	Peach aldehyde	M/s Sonebon Laboratories, Kottayam-5.	Non-exclusive.
8.	tert-Butylcatechol	M/s Percynic Chemicals, Bombay-1.	Non-exclusive.

A-III SPONSORED PROJECTS CONCLUDED DURING 1970-71

	Project	*Sponsor*
1.	Butylated hydroxyanisole (BHA)	M/s Mhatre's Art Studio, Bombay-57.
2.	Carbimazole	M/s Indian Schering Ltd., Bombay-71.
3.	Coumarin	M/s Lona Industries (P) Ltd., Ladivali, Dist. Kolaba.
4.	New Ingrain dyes	M/s Lona Industries (P) Ltd. Ladivali, Dist. Kolaba.

5.	Infrared spectrophotometer	M/s Swastik Rubber Products, (P) Ltd., Poona.
6.	Maleic anhydride by the oxidation of benzene	M/s Aniline Dyestuffs and Pharmaceuticals Ltd., Bombay.
7.	Methyl vinyl ether-maleic anhydride copolymer	M/s Indian Detonators, Hyderabad.
8.	Quinacridone pigment	M/s Lona Industries(P) Ltd. Ladivali, Dist. Kolaba.
9.	Testing methods for ceramic compositions	M/s Philips India Ltd., Loni Kalbhor, Poona.
10.	Chemical and thermodynamic properties of refractory materials at high temperature	U.S. Deptt. of Commerce, Washington, (PL-480 scheme).

A-IV TRAINING

During the period under review following scientists from universities, industries and research institutes were trained :

	Name of the trainee and place	*Field of training*
1.	Miss K. Geetharani Kavu, I. I. T., Madras.	Radiation dosimetry.
2.	Dr. V. S. Jatkar, Deptt. of Chemistry, Wadia College, Poona.	Use of radioactive isotopes in physico-chemical research.
3.	Mr. V. K. Verma, Deptt. of Chemistry, Punjab University, Chandigarh.	Use of Mössbauer spectroscope in coordination chemistry.
4.	Dr. K. Appalacharyulu, Radio-Isotope Lab., P & D Divn., F. C. I., Sindri.	Working of Mössbauer spectrometer.
5.	Mr. S. V. Patil, Dept. of Chemistry, Karnatak University, Dharwar.	Physico-studies of some inorganic complexes.

6.	Mr. A. K. S. Baru, R. R. L., Jorhat.	Microanalysis.
7.	Mr. K. T. Borkhade, Science College, Amraoti.	
8.	Mr. P. A. Abraham, Saugar University, Saugar.	
9.	Mr. R. Deshpande, I. D. P. L., Hyderabad.	
10.	Mr. Jacob, Saugar University, Saugar.	Isolation and characterization of natural products.
11.	Dr. C. K. Oza, Rajasthan University, Jaipur.	Light scattering.
12.	Dr. J. K. Karandikar and Mr. S. L. Kate, B. J. Medical College, Poona.	Polyacrylamide gel electrophoresis techniques.
13.	Mr. G. Chandra Sekharappa, Mysore University, Mysore.	Microbiology.
14.	Miss Hema Pant, Birla Institute of Technology & Science, Pilani.	Microbiology.
15.	Mr. H. Sayyad, Ruby Hall, Poona.	Vitamin B_{12} estimations.
16.	Mr. Kapadi, M/s Tata Chemicals, Mithapur.	Glass blowing techniques.

A-V SEMINARS AND LECTURES

Problems of Transition from Laboratory Research to Industrial Application–UNESCO Seminar

This laboratory was the venue of a seminar on the 'Problems of Transition from Laboratory Research to Industrial Application', organized under the joint auspices of the UNESCO and the CSIR. Thirty-two scientists from 14 Asian and other countries participated in the seminar which extended for six days from December 9, 1970. Dr. Atma Ram, Director General, CSIR, inaugurated the proceedings while Dr. B. Oberbacher (Batelle Institute, E. V., Frankfurt, Fed. Rep. of Germany), Dr. E. S. Shanley (Arthur D. Little, Inc. Cambridge, Mass., U. S. A.), and Prof. B. D. Tilak (NCL, Poona) directed the seminar.

Dr. V. P. Kahr, Deputy Director, Field Science Office for South Asia, UNESCO, New Delhi, outlined the purpose in organising the seminar.

The importance of R and D work to accelerate industrial and economic growth is now well recognised. Nevertheless, in developing countries of Asia, problems of technology transfer are variegated. 31 papers sent by the participants served as a background for more exhaustive discussion held in three sessions. Extensive discussions centred around: prerequisites to successful industrial research; rationale of technology development and the transition of laboratory research to industry, and transition of laboratory/pilot plant research/development to industry.

Several recommendations were made for proper and balanced development of R and D work in private and public undertakings in developing countries through self-generated resources and international assistance.

English and Marathi Press and technical journals gave wide coverage for the seminar. The support papers and proceedings of the seminar will be published shortly.

Recent Advances In Heterocyclic Chemistry-Seminar

A seminar on the 'Recent advances in heterocyclic chemistry', was held at NCL on 7th and 8th September, 1970. The seminar consisted of 14 invited lectures. Four scientists from NCL and 10 from other important research schools participated in the seminar. The seminar provided a unique opportunity to chemists working in this field to present their work and to exchange ideas with others. Some 60 scientists from university departments, research institutes and industrial establishments participated in the seminar. The speakers included Profs. C. N. R. Rao, P. T. Narasimhan, M. V. George, V. R. Srinivasan; Drs. H. Singh, S. V. Kessar, T. R. Kasturi, Nitya Anand, M. D. Nair, Nagabhusan Rao, and Drs. K. G. Das, P. M. Nair, V. N. Gogte and Miss H. V. Berde from the NCL.

The seminar was divided into 4 technical sessions. One session was devoted to physical and spectroscopic aspects of heterocyclic chemistry. The topics included: donor properties and electronic structure of some heterocyclic compounds and their PMR and mass spectral characteristics. The other three sessions were devoted to the synthetic aspects of heterocyclic chemistry.

Amongst the topics discussed were synthesis of nitrogen heterocyclics by rearrangement reactions, synthesis of various oxygen heterocyclics, trancyclization reactions heterocyclic steroids, cycloaddition reaction leading to heterocyclics and some thermal and photochemical transformations of heterocyclic compounds.

Lectures

In addition to the talks by several NCL scientists in weekly seminars, the following lectures were delivered by visiting scientists :

1.	**Prof. F. Marta, University of Szeged, Hungary.**	**Interpretations of limiting rate and of induction period in oxidation of benzaldehyde catalized by cobaltous acetate.**
2.	Dr. R. C. Pandey, University of Illinois, USA.	Structural studies of the macrolide antibiotic tetrin A.
3.	Prof. K. Vedam, Pennsylvania State University, University Park, USA.	(i) Optical characterization of surfaces and opaque materials by ellipsometry. (ii) Piezo-optic properties of solids under high pressure.
4.	Prof. James Diefendrfer, Lehigh University, Pennsylvania, USA.	NMR hydrogen bonding.
5.	Dr. R. J. Ackermann, Argonne National Laboratory, Argonne, USA.	The energetic and structure vapour condensed phase equilibria; the effects on non-stoichiometry on vaporization behaviour and thermodynamic properties.
6.	Dr. Abdulali Tapia, Bombay.	Synthesis of optically active urobilin III and other researches in the chemistry of bile pigments.
7.	Mr. M. A. Winkler, University of Surrey, U. K.	Industrial waste disposal.
8.	Dr. Jayant Bapat, Caufield Institute of Technology, Melbourne, Australia.	A new synthesis of the tropane system.

9.	Prof. R. Haffmann, Cornell University, Ithaca, USA.	(i) Orbital symmetry control of chemical reactions (3 lectures). (ii) Stereochemical consequences of concerted cycloaddition.
10.	Prof. Dr. Otto Horn, Far Hoechst AG, West Germany.	(i) Petrochemistry and petrochemicals. (ii) Natural and synthetic polymers.
11.	Prof. I. D. Rattee, University of Leeds, UK.	(i) Theory and practice of dyeing with reactive dyes. (ii) Steric effects and dye adsorption.
12.	Prof. F. W. Bachelar, University of Calgary, Canada.	Mechanism of Darzens glycidic ester condensation.
13.	Prof. C. N. N. Rao, I. I. T., Kanpur.	(i) Structure of water. (ii) Localized collective electron transitions in oxides.
14.	Dr. G. S. Sidhu, R. R. L., Hyderabad.	(i) Naturally occurring napthols and napthoquinones from diospyros series. (ii) Contribution to industry by R. R. L., Hyderabad.

Following NCL scientsits delivered lectures at various institutes, universities, colleges, etc.

	Name of the scientist	*Subject*	*Venue*
1.	Dr. K. G. Das	Organic mass spectrometry (2 lectures).	Central Drug Research Institute, Lucknow.
2.	Dr. L. K. Doraiswamy	(i) Chemical reactor design.	Regional Engineering College, Warangal.
		(ii) Applications of chemical reaction engineering at NCL.	Laxminarayan Institute of Technology, Nagpur.

		(iii) Some recent developments in chemical reaction analysis.	M. S. University, Baroda.
3.	Dr. V. Jagannathan	(i) Brain metabolism (2 lectures). (ii) Enzyme kinetics (2 lectures).	Indian Institute of Science, Bangalore. Central Food Technological Res. Institute, Mysore.
4.	Mr. V. S. Krishnamachar	Microbiology (5 lectures).	Ahmednagar College, Ahmednagar.
5.	Mr. P. S. Kulkarni	Nuclear chemistry (10 lectures).	N. Wadia College, Poona.
6.	Dr. (Miss) S. B. Kulkarni	Surface chemistry (10 lectures).	N. Wadia College, Poona.
7.	Mr. A. F. Mascarenhas	Plant tissue culture.	Ahmednagar College, Ahmednagar.
8.	Dr. H. B. Mathur	Mössbauer effect studies and their application to chemistry.	Indian Science Congress, Banglaore.
9.	Dr. M. N. S. Murthy	Quantum chemistry (14 lectures).	N. Wadia College, Poona.
10.	Dr. Gopal Pathak	Chemical thermodynamics and statistical thermodynamics (21 lectures).	N. Wadia College, Poona.
11.	Dr. A. V. Rama Rao	Applications of spectroscopy in biochemical analysis.	Ahmednagar College, Ahmednagar.

12.	Dr. P. N. Rangachari	Contributions of Dr. H. G. Khorana, leading to the synthesis of the gene.	Ahmednagar College, Ahmednagar.
13.	Dr. A. S. Rao	Stereochemistry (4 lectures).	Ahmednagar College, Ahmednagar.
14.	Dr. C. SivaRaman	(i) Regulation of enzyme action. (ii) Allosteric enzymes (3 lectures).	Ahmednagar College, Ahmednagar.
15.	Dr. P. R. SubbaRaman	(i) Ion exchange and solvent extraction in trace analysis.	Indian Science Congress, Bangalore.
		(ii) Modern instrumental methods of analysis (4 lectures).	S. P. College, Poona.
16.	Dr. S. S. Tavale	Molecular structure by X-ray diffraction (3 lectures).	N. Wadia College, Poona.
17.	Dr. B. D. Tilak	(i) Rationale of industrial research and the problems of its transition to industry.	Indian Rubber Manufacturers' Res. Association Seminar, Bombay.
		(ii) Work in progress at NCL.	Annual general meeting of the Textile Auxiliaries Manufacturers' Association, Bombay.

A-VI STAFF NEWS

1. *Foreign deputations / training, etc.*

   (i) Dr. V. J. Rao proceeded to U. K. under Colombo Plan for training in the field of 'Solid state materials', for one year (October 1970 to September 1971).

   (ii) Dr. Sukh Dev visited University of Oklahoma, Department of Chemistry, Oklahoma, U.S.A., as a visiting professor (August 1970 to March 1971).

   (iii) Dr. K. Venkataraman attended a symposium on 'Wood extractives', under the auspices of the American Chemical Society in Los Angeles, U.S.A., where he delivered a plenary lecture on 'Chemotaxonomy of *Moraceae*'. During his stay in U.S.A., he visited various universities, industries, research institutions and gave series of lectures. He also visited Hungarian Academy of Sciences, Budapest, Hungary and Japan Dyestuff Industries' Association, Tokyo, Japan (March/June 1971).

2. *Participation of NCL scientists in seminars*

	Symposia, seminar, etc., and venue	*Name of the scientist*
1.	Indian Science Congress, Bangalore.	Dr. H. B. Mathur, Dr. P. R. SubbaRaman
2.	Seminar on 'Ultrasonics and their chemical applications', Allahabad University, Allahabad.	Dr. P. Roy Chowdhury
3.	Convention of Chemists, I. I. T., Madras.	Dr. K. G. Das, Dr. V. N. Gogte
4.	Symposium on 'Recent advances in heterocyclic chemistry', NCL, Poona.	Dr. B. D. Tilak, Dr. V. N. Gogte, Dr. P. M. Nair, (Miss) H. V. Berde, Dr. K. G. Das
5.	5th IRMRA technical seminar, Bombay.	Dr. S. L. Kapur, Dr. S. Gundiah

6.	Annual meeting of the Indian Institute of Chemical Engineers, Hyderabad.	Dr. L. K. Doraiswamy
7.	Conference on 'R & D in industry', organized by Industrial Credit & Investment Corpn. of India, Bombay.	Dr. L. K. Doraiswamy
8.	Conference on ' The use of pilot plants, ' organized by Indian Institute of Chemical Engineers, Bombay.	Dr. L. K. Doraiswamy
9.	ISI 7th sectional committee (EDC-57) meeting, Madras.	Dr. L. K. Doraiswamy
10.	Symposium on 'Molecular mechanism of drug action,' CDRI, Lucknow.	Dr. B. V. Ramchandran
11.	Guha Research Conference, Mercara, Coorg.	Dr. C. SivaRaman
12.	Second 'International convention of Biochemists', Baroda.	Dr. P. N. Rangachari
13.	UNESCO sponsored training course on 'Chemistry of natural products', University of Delhi, New Delhi.	Dr. A. B. Upadhya
14.	Bombay University sponsored course on 'Chemical process economics', Bombay University, Bombay.	Mr. M. N. Krishnamurthy, Mr. C. U. Saraf

3. *Awards and Honours*

1. Dr. L. K. Doraiswamy was awarded the 'Dr. K. G. Naik Gold Med by the M. S. University of Baroda for the year 1970.
2. Dr. K. Venkataraman was elected as an 'Honorary Member' of t Polish Chemical Society, Poland.

4. *Post graduate degrees received by NCL staff and research fellows*

Name	*Degree*	*University*
Bakshi, S. H.	Ph. D.	Bombay
*Deshpande (Mrs.), N. R.	Ph. D.	Poona
Dixit, S. S.	Ph. D.	Bombay
Nambiar, O. G. B.	Ph. D.	Kerala
Potnis, G. V.	Ph. D.	Poona.
*Sathe (Miss), R. N.	Ph. D.	Poona
Shet, S. G.	Ph. D.	Poona

* These are research fellows.

5. *NCL scientists recognized by different universities as research guides*

Dr. Ayyangar, N. R.	Poona.
Dr. Bose, J. L.	Bombay, Poona, Nagpur, Shivaji
Dr. Chakravarti, K. K.	Poona, Shivaji, Karnatak
Dr. Dadape, V. V.	Bombay, Poona, Karnatak, Vikram., Banaras
Dr. Damodaran, V.	Shri Venkateswara University, Tirupathi
Dr. Das, K. G.	Poona, Bombay, Kerala
Dr. Doraiswamy, L. K.	Poona, Bombay, Nagpur, Calcutta, Jadavpur
Dr. Ghatge, B. B.	Poona
Dr. Ghatge, N. D.	Poona, Bombay, Shivaji
Dr. Gogte, V. N.	Shivaji
Dr. Goswami, A.	Calcutta, Poona, Punjab
Dr. Gupta, J.	Bombay, Poona, Punjab, Madras
Dr. Ingle, T. R.	Poona.

Dr. Jagannathan, V.	Bombay, Poona
Dr. Joshi, R. M.	Poona
Dr. Kapur, S. L.	Bombay, Poona, Punjab
Dr. Katti, S. S.	Bombay
*Dr. Kelkar, G. R.	Poona
Dr. Kulkarni (Miss), S. B.	Poona
Dr. Kulkarni, S. N.	Poona, Bombay, Karnatak, Shivaji
Dr. Mathur, H. B.	Poona, Agra, Madras, Bombay, I.I.T., Bombay
Dr. Nair, P. M.	Poona, Shivaji, Andhra
Dr. Narayanan, C. R.	Poona, Bombay, A. B. Uni., Zaria, Nigeria
Dr. Pai, M. U.	Bombay
Dr. Pant, L. M.	Poona
Dr. Ramchandran, B. V.	Shivaji, Poona
Dr. Rama Rao, A. V.	Shivaji
Dr. Rangachari, P. N.	Poona, Shivaji
Dr. Rao, A. S.	Poona, Shivaji
Dr. Roy Chowdhury, P.	Marathwada
Dr. Sadana, J. C.	Poona, Aligarh
Dr. Sen, D. N.	Poona, Bombay
Dr. Sinha, A. P. B.	Poona, Banaras, Vikram, Andhra, Bombay
Dr. SivaRaman, C.	Poona
Dr. SubbaRaman, P. R.	Poona, Bombay, Gujarat, Kerala
Dr. Sukh Dev	Poona, Bombay, Agra, Punjab, I. I. Science, Bangalore

Dr. Tilak, B. D.	Bombay, Poona
*Dr. Venkataraman, K.	Poona, Bombay, Madras, Banaras

*Retired

6. *NCL scientists working as institutional consultants*

1.	Dr. Chakravarti, K. K.	M/s Sunanda Aromatic Industries, Mysore.
2.	Dr. Ghatge, N. D.	M/s Swastik Rubber Products (P) Ltd., Poona.
3.	Dr. Mitra, R. B.	M/s Alta Laboratories (P) Ltd., Khopoli.
4.	Dr. Rama Rao, A. V.	M/s Poona Synthetics, Poona
5.	Dr. Sukh Dev	M/s Camphor & Allied Products Ltd., Bareilly.
6.	Dr. Tilak, B. D.	(i) M/s Aniline Dyestuffs & Pharmaceuticals Ltd., Bombay (ii) M/s Indian Dyestuff Industries Ltd., Kalyan.

CSIR share on account of technical consultancy	Rs. 19,433/-

A-VII PUBLICATIONS

Research Papers

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2. Das, K. G.
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2. Roy Chowdhury, P.
   Adiabatic compressibility of polyelectrolytes.
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A-VIII PATENTS IN FORCE

Patents sealed

1. **56726***
   Preparation of water dispersible DDT as an oil bound paste.
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17. **71190***
Preparation of anion exchange resins.
Krishnaswamy, N., Govindan, K. P. and Dasare, B. D.

18. **73702**
A process for the preparation of cyclopentadecanolide (exaltolide).
Dhekne, V. V., Ghatge, B. B. and Bhattacharyya, S. C.

19. **74356***
Preparation of insoluble reaction products of polystyrene for use as cation exchange materials.
Govindan, K. P. and Krishnaswamy, N.

20. **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.

21. **77225***
A process for the preparation of β-ionone from pseudoionone.
Joshi, B. N., Chakravarti, K. K., Shah, R. C. and Bhattacharyya, S. C.

22. **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.

23. **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.

24. **86991***
Preparation of polyurethane printing rollers.
Ghatge, N. D. and Kapur, S. L.

25. **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.

26. **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.

27. **98156***
Preparation of solvent modified copolymers of vinyl monomers in bead form.
Kapur, S. L. and Ramakrishnan, K..

28. **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.

29. **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.

30. **109489**
Production of aryl-glycosides.
Ingle, T. R. and Bose, J. L.

31. **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

32. **113406**
A new thermistor composition exhibiting high positive temperature coefficient of resistivity (posistor).
Brahmecha, B. G. and Sinha, K. P.

33. **116453**
Disperse dyes for polyesters with good affinity and sublimation fastness.
Raman, S. K. and Tilak, B. D.

34. **116675**
Improvements in or relating to polymers possessing polyamide linkages for plastics, fibres and like industrial applications.
Ghatge, N. D., Patil, S. B. and Patil , V. S.

35. **117210**
A direct process for the manufacture of dibutylin di-iodide and of the oxide therefrom.
Gupta, J., Gopinathan, C., Gopinathan (Mrs.), S. and Awasarkar,P.A.

36. **117403**
Preparation of water thinnable emulsion paints from linseed oil.
Kapur, S. L. and Bakshi, S. H.

37. **118476**
Methods of preparing isocyanates, mono and polyureas from pentadecenyl phenol (anacardol).
Ghatge, N. D. and Yadav, S. D.

* These patents (22) are being commercially exploited.

Patents filed

1. **67513**
   Improvements in or relating to the separation of niobium and tantalum from each other by liquid-liquid extraction.
   Sarma, B. and Gupta, J.

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. **113703**
   Improvements in or relating to magnesium zinc ferrites.
   Krishna Rao, V. V., Kanade (Miss), S. B. and Sinha, A. P. B.

5. **113825**
   11 ORT nickel zinc ferrites.
   Krishna Rao, V. V., Kanade (Miss), S. B. and Sinha A. P. B.

6. **121538**
   A process for the shellac-polyester urethane compositions for use in textiles, water proofing adhesives, paints and varnishes and in electrical insulating varnishes.
   Ghatge, N. D. and Srinivasan, S. R.

7. **123638**
   Improvements in or relating to the manufacture of cashewnut shell gum (CNS-gum).
   Ingle, T. R., Vaidya, S. H. and Pai, M. U.

8. **125138**
   Method of preparing polyisocyanates and polyureas from pentadecenyl phenol (anacardol').
   Ghatge, N. D. and Mahajan, S. S.

9. **126354**
A process for obtaining useful steroids from a new plant source.
Sukh Dev, Patil, V. D. and Nayak, U. R.

10. **126393**
An improved method for the manufacture of calcium hypophosphite.
Goswami, M., Lobo, J. and Brahme, P. H.

11. **127743**
A process for obtaining colchicine from a new plant source.
Kapadia, V. H., Sukh Dev and Rao, R. S.

12. **127750**
A process for production of pyridoxine hydrochloride.
Joshi, C. G. and Sukh Dev.

13. **130254**
A process for the manufacture of valcanizable graft-copolymer of chlorosulfonyl polyethylene with maleic anhydride (and its substituted analogues) for use as a synthetic rubber and as a base in coating compositions.
Joshi, R. M.

14. **130551**
A new process for separation of the dimethyl and monomethyl components from a mixture of dimethyl dichlorosilane and methyl trichloro-silane
Gupta, J., Gopinathan, C., Gopinathan (Mrs.), S., Eapen, M. J. and Awasarkar, P. A.

A-IX TABLE I : PRODUCTS MANUFACTURED ON THE BASIS OF NCL KNOW-HOW

T = Metric tonnes

S. No.	Name of the process & Indian Patent	Field of utilization	Name of the manufacturer (year of commencement of production)	Production 1970-71 Qty./Value in Rs. lakhs	Production Upto March 1970 Qty./Value in Rs. lakhs	Remarks
1	2	3	4	5	6	7
1.	Acetanilide	Intermediate	M/s Hindustan Organic Chemicals Ltd., Rasayani, through project engineers M/s R. L. Dalal & Co., Bombay-18 (1969).	964 T 60·89	247 T 15·54	Exclusive to the project engineer.
2.	Acriflavine (sponsored)	Pharmaceuticals	M/s Western India Fine Chemicals, 83, Lalbahadur Shastri Marg, Bombay-80 (1969).	905 kg. 4·15	847 kg. 3·67	Exclusive.
3.	Adhesives for decorative laminates (sponsored)	Laminates	M/s Swastik Rubber Products Ltd., Poona-3 (1969).	18·75 T 1·88	12 T 1·02	Exclusive.
**4.	Anion exchange resin from melamine (71190)	Demineralization of liquids	M/s Tulsi Industries, Hadapsar Industrial Estate, Poona-13 (1963).	—	565 cft. 1·75	Non-exclusive.
5.	Antipriming compositions (77081)	Antipriming in locomotives	Research, Design and Standard Organisation, M & C Wing, Chittaranjan (1964).	11 T 0·33	78·70 T 1·99	Non-exclusive.

1	2	3	4	5	6	7
6.	Bacterial diastase (66096)	Textile desizing	M/s Chemaux (P) Ltd., Mahim, Bombay-16 (1967).	223 T 6·69	125·58 T 4·62	Exclusive.
7.	Benzoic acid (sponsored)	Pharmaceuticals	M/s Aniline Dyestuffs & Pharmaceuticals (P) Ltd., 28, Apollo street, Bombay-1 (1969).	—	— 0·17	Exclusive. Experimental trials started.
8.	Berberine hydrochloride (sponsored)	Pharmaceuticals	M/s G. Vallabhadas & Co., 180/82, Samuel Street, Bombay-9 (1965).	6 T 12·00	0·30 T 0·36	Exclusive.
*9.	*Cadmium sulphide photoconductive cells*	*Electronics*	(*i*) *M/s Chinoy Electronics,* 64, Koregaon Park, Poona-1 (1971).	—	—	Non- exclusive. Released in Feb. 1971. Trial Production started.
		**	(ii) M/s Gera Engineering Co., 8/352, Boat Club Road, Poona-1 (1969).	— 0·50	—	Non-exclusive.
10.	Calcium hypophosphite (sponsored)	Pharmaceuticals	M/s Hypophosphite & Co., 79-F, Princess Street, Bombay-2 (1967).	11 T 6·0	12·25 T 6·30	Exclusive.
11.	Calcium silicate (sponsored)	Low density insulators	M/s Newkem Products Corp., Harganga Mahal, Bombay-14 (1968).	181 T 6·4	322 T 11·40	Exclusive.

1	2	3	4	5	6	7
12.	Can sealing composition (66194)	Metal can industry	M/s Arya Chemical Works, 114/2A, Dharmatolla Street, Calcutta-13 (1962).	24·5 T 1·50	133 T 6·98	Exclusive.
*13.	Carbimazole (sponsored)	Pharmaceuticals	M/s Indian Schering Ltd., Sion-Trombay Road, Chembur, Bombay-71 (1970).	10 kg. 0·83	—	Exclusive.
**14.	Cation exchange resin from CNSL (59497, 59606)	Demineralization of liquids	M/s Tulsi Industries, Poona-13 (1960).	—	7,310 cft. 6·14	Exclusive.
15.	Chloral hydrate	Industrial chemicals	M/s Hindustan Insecticides Ltd., Industrial Area, New Delhi-15 (1963).	0·45 T 0·046	19·46 T 1·89	Exclusive.
16.	Coating for oil filter papers	Oil filtration	M/s White Cloud Paper Mills, 412, Gultekdi Road, Poona-9 (1968).	—	—	Non-exclusive. Technical aid. Trial production started.
**17.	DDT-water dispersible (56726)	Insecticides	M/s Lotus Industries, 62/20, Luz Church Road, Madras-4 (1967).	—	0·89 T 0·08	Non-exclusive.
*18.	Diethyl-*m*-aminophenol (sponsored)	Dye intermediate	M/s Sahyadri Dyestuffs and Chemicals (P) Ltd., 117, Vithalwadi Road, Poona-9 (1970).	4 T 2·40	—	Exclusive.

1	2	3	4	5	6	7
19.	Dihydroisojasmone	Perfumery	M/s S. H. Kelkar & Co. (P) Ltd., Bombay-Agra Road, Bombay-80 (1965).	152 kg. 0·51	445 kg. 1·54	Non-exclusive. Technical aid.
20.	Ethylene oxide condensates (sponsored)	Surface active agent	M/s Hico Products (P) Ltd., Mogal Lane, Bombay-16 (1965).	329 T 46·45	1,110 T 119	Exclusive.
21.	Ferrites (hard)	Electronics	M/s Semiconductors Ltd., Nagar Road, Poona-14 (1968).	—	—	Non-exclusive. Production started recently.
*22.	Geraniol, citronellal and citronellol (sponsored)	Perfumery	M/s Radhakishan Rajaram & Co., 141, Samaldas Gandhi Marg, Bombay-2 (1970).	2 T 2·60	—	Exclusive.
23.	Hexylresorcinol (57888)	Pharmaceuticals	M/s Unichem Laboratories Ltd., Jogeshwari, Bombay-60 (1964).	83·40 kg 0·346	13 kg. 0·08	Exclusive.
24.	4-Hydroxycoumarin (62890, 63083)	-do-	-do- (1964).	82·7 kg. 0·178	265 kg. 0·81	Exclusive.
**25.	Heat sealable coating composition	Adhesives	M/s Chandmal Fakirchand Jain, Khajuri Bazar, Indore-2 (1963).	—	—	Non-exclusive. Technical aid.

1	2	3	4	5	6	7
26.	β-Ionone (77225)	Perfumery Pharmaceuticals	**(i) M/s S. H. Kelkar & Co. (P) Ltd., Bombay (1964).	—	—	Non-exclusive. The firm is producing the item.
			(ii) M/s Industrial Perfumes Ltd., Army & Navy Bldg., M. G. Road, Fort, Bombay-1 (1968).	22·39 T 14·65	12·64 T 8·21	Non-exclusive. The firm has processed 22·30 T of β-ionone for M/s Roche Products Ltd., Bombay.
**27.	Liquid rubber (60555)	Adhesives, Rubber rollers	M/s K. N. Chari & Co., 144, Nyneappa Naick, Street, Madras-3 (1962).	—	2·2 T —	Non-exclusive. Production for captive use.
*28.	Orthotolyl biguanide	Soap	M/s Industrial Perfumes Ltd., Bombay-1 (1970).	2·75 T 0·74	—	Exclusive.
29.	Perfumery products based on Longifolene (Capinone) (sponsored)	Perfumery	M/s Camphor & Allied Products, Bareilly (1968).	3·37 T 3·21	13·71 T 10·46	Exclusive.
30.	Perfumery products based on Δ^3-Carene (Meracene) (sponsored)	-do-	-do- (1968).	1·87 T 0·68		

1	2	3	4	5	6	7
31.	*l*-Menthol from dementholized peppermint oil (sponsored)	Fine Chemicals, Drugs	M/s Bhavana Chemicals Ltd., Laxmi Insurance Bldg., Bombay-1 (1968).	—	—	Exclusive. Experimental adoption of work in progress.
32.	Nicotine sulphate (54876, 83716)	Insecticides	M/s Urvakunj Tobacco By-products Ltd., Dharmaj (Dist. Kaira) (1963).	2 T 0·32	25·81 T 4·12	Exclusive on zonal basis
33.	Peach aldehyde	Perfumery	M/s S. H Kelkar & Co., (P) Ltd., Bombay (1965).	0·69 T 1·32	2·48 T 4·36	Non-exclusive. Technical aid.
34.	β-Phenethyl alcohol (sponsored)*	Perfumery	M/s Sunanda Aromatic Industries, K. R. S. Road, Mettagalli, Mysore (1970).	9 T 3·15	—	Exclusive.
35.	Phthalates-dioctyl and dibutyl	Plasticizers	(i) M/s Alta Laboratories Ltd., Giri Vihar, Khopoli (Dist. Kolaba) (1969).	736·2 T (DOP) 54·5	198 T(DOP) 14·69	Non-exclusive.
			*(ii) M/s India Carbon Ltd., Shiv Sagar Estate, Dr. A. B. Road, Worli, Bombay-18 (1971).	318 T (DOP) 24·17	—	Non-exclusive.

1	2	3	4	5	6	7
*36.	Phthalates-diethyl and dimethyl	Plasticizers	M/s Mysore Acetate and Chemicals Co., Ltd., 'Mysugar Buildings', Sri J. W. Road, Bangalore-2 (1970).	48·62 T (DEP) 3·72	—	Non-exclusive.
**37.	Polyurethane printing rollers (86991)	Printing	(i) M/s Saraswathy Printing Press, 32, Acharya P. C. Road, Calcutta-9 (1965).	—	—	Non-exclusive.
			(ii) M/s Dabholkar Bros. East Street, Poona-1 (1965).	—	—	Non-exclusive.
*38.	Radio opaque dyes (sponsored)	Pharmaceuticals	M/s Unichem Laboratories, Bombay-26 (1970).	—	—	Exclusive. Trial production amounting to 7·7 kg. has been done.
39.	Rigid filters (59608, 66966)	Tube wells	M/s Ashim Filters, 196, Defence Colony, New Delhi (1965).	570 Mtrs. 1·29	4,705 Mtrs. 8·97	Exclusive.
**40.	Rubber base contact adhesive (65977)	Adhesives	M/s K. N. Chari & Co., Madras-3 (1962).	—	16,925 Ltrs. 1·37	Non-exclusive.
41.	Rubber blowing agent	Rubber chemicals	M/s Swastik Rubber Products Ltd., Poona-3 (1968).	34 T 4·78	59 T 6·92	Non-exclusive. Technical aid.

1	2	3	4	5	6	7
42.	Rubberized cork sheet	Gaskets	M/s Bharat Casements (P) Ltd., P. B. No. 89, Baroda (1966).	16·27 lakh Nos. 5·02	16·40 lakh Nos. 5·86	Non-exclusive.
43.	Rubber reclaiming agent	Rubber chemicals	M/s Swastik Rubber Products Ltd., Poona-3 (1968).	4·39 T 0·57	8·93 T 1·09	Non-exclusive.
44.	Silica gel (sponsored)	Humidity control	M/s Minco Products, 301/27, T H. Road, Madras-21 (1963).	10 T 0·85	62 T 3·98	Exclusive.
45.	Sisal wax (64958, 65440)	Cosmetics, Polishes	M/s Aphali Pharmaceuticals Ltd., Station Road, Ahmednagar (1966).	—	15·30 T 1·64	Non-exclusive.
46.	Sorbide nitrate (sponsored)	Pharmaceuticals	M/s Indian Schering Ltd., Bombay-1 (1969).	107 kg. 1·47	130 kg. 3·90	Exclusive.
**47.	Styrene DVB-base cation exchange resin (65976, 98155, 98156)	Demineralization of liquids	M/s Industrial & Agricultural Engg. Co. (P) Ltd., 43, Forbes Street, Bombay-1 (1967).	—	—	Non-exclusive.
48.	Thermistors	Electronics	(i) M/s Semiconductors Ltd., Poona-14 (1963).	4·77 lakh Nos. 3·54	25·62 lakh Nos. 23·74	Non-exclusive. Technical aid.

1	2	3	4	5	6	7
			(ii) M/s Tempo Semiconductors, Vile Parle (E), Bombay-57 (1963)	10,000 Nos. 0·40	25,000 Nos. 1·01	Non-exclusive. Technical aid.
**49.	Titanium tetrachloride (sponsored)	Industrial chemicals	M/s Travancore Titanium Products Ltd., Trivandrum-7 (1967).	—	0·82 T 0·06	—
50.	Vapour phase chromatograph	Instruments	M/s Associate Instruments Manufacturers (India) P. Ltd., 26-27, Asaf Ali Road, New Delhi (1969).	21 Units 4·20	17 Units 3·35	Exclusive. Value is excluding the cost of imported components.
51.	Warfarin	Rodenticides	M/s Unichem Laboratories, Bombay (1968).	33·4 kg. 0·195	67 kg. 0·40	Exclusive.

* During 1969-70, 44 products were manufactured on the basis of NCL know-how, while during the period under review, production has been commenced on these 7 new items.

** These firms have not furnished production figures for the current year even after repeated requests.

Table—1 Continued.

Value of some major chemicals produced in Fine Chemicals Project :

		Value in Rs.
52.	Alumina (for column chromatography)	17,010/-
53.	'Chembond'	23,400/-
54.	Chlorodimethyl ether	11,400/-
55.	Silica gel (column chromatography & TLC)	83,565/-

VALUE OF PRODUCTION BASED ON NCL KNOW-HOW

Year	No. of items manufactured (including major FCP items)	Value of production (Rs. in lakhs)
Up to 1967	26	53·22
1967—68	29	39·98
1968—69	47	69·55
1969—70	53	130·22
1970—71	55*	283·84
	Total	576·81

* Five items were dropped from the FCP production programme and 7 items were newly added during the year.

Foreign Exchange Saving

Majority of the above items have led to import substitution. Assuming 40% of above production as F. E. saving, the cumulative F. E. saving due to industrial production (1952-1971) based on NCL know-how amounts to about Rs. 225 lakhs.

A-X TABLE II (A) : PROCESSES RELEASED AND AWAITING PRODUCTION

S. No.	Name of the process and Indian Patent No.	Field of utilization	Name of the party & year of release	Nature of licence/present state of development
1	2	3	4	5
1.	Aniline	Industrial chemicals	M/s Hindustan Organic Chemicals Ltd., Rasayani, through project engineers-M/s Engineers India Ltd., New Delhi (1969).	Exclusive agreement for engineering the project.
2.	BD-catalyst (sponsored)	Catalyst for synthetic rubber	M/s Synthetic and Chemicals Ltd., 284, Frere Road, Bombay-1 (1969).	Exclusive.
3.	Butyl titanate	Varnishes & enamels	M/s Synthochem, 33-A, Laxmi Nagar, Indore-1 (1970).	Non-exclusive. Agreement in progress.
4.	Butylated hydroxyanisole (sponsored)	Antioxidant	M/s Mhatre Art Studio, Mahant Road, Vile Parle, Bombay-57 (1970).	Exclusive.
5.	Catechol	Pharmaceuticals	M/s Percynic Chemicals, United Bank of India Building, Sir P. M. Road, Bombay-1 (1970).	Non-exclusive. Plant installation in progress.

1	2	3	4	5
6.	Cation exchange resin polystyrene base (74356)	Demineralization of liquids	M/s Tulsi Industries, Poona-13 (1965).	Non-exclusive.
7.	Chlorinated copper phthalocyanine (sponsored)	Dye intermediate	M/s Sudarshan Chemical Industries (P) Ltd., 162, Wellesley Road, Poona-1 (1968).	Exclusive. Pilot plant trials in progress.
8.	Chloromethanes	Industrial chemicals	M/s Standard Mills Co. Ltd., (Chemicals Division) P. B. No. 1038, Bombay-20 (1969).	Semi-commercial (300 TPA, plant commissioned at the works.
9.	Chlorobenzenes (sponsored)	Industrial chemicals	M/s Hindustan Organic Chemicals Ltd., Rasayani (1969).	Exclusive.
10.	Coumarin (sponsored)	Perfumery	M/s Lona Industries (P) Ltd., Ladivali, Taluka-Panvel, Dist. Kolaba (1970).	Exclusive,
11.	Covering materials from CNSL (74451)	Chemical resistant flooring	M/s Natson Manufacturing Co., Bhadra, Ahmedabad (1964).	Exclusive.
12.	Dithranol	Pharmaceuticals	M/s Indian Dyestuffs Industries Ltd., Kalyan (1968).	Exclusive.

1	2	3	4	5
13.	Hexachloroethane	Industrial chemicals	M/s Industrial Oxygen (P) Ltd., Off Nagar Road, Poona-14 (1971).	Non-exclusive. Agreement in progress.
14.	8-Hydroxyquinoline (sponsored)	Pharmaceuticals	M/s Alta Laboratories Ltd., Khopoli (1970).	Exclusive.
15.	Isolation of borneol (sponsored)	Perfumery	M/s Camphor & Allied Products, Bareilly (1969).	Exclusive.
16.	Liquid stabilizer for PVC (sponsored)	Plastics	M/s Swastik Rubber Products Ltd., Poona-3 (1969).	Exclusive.
7.	Megimide (sponsored)	Pharmaceuticals	M/s Indian Schering Ltd., Bombay-1 (1969).	Exclusive.
18.	Nonylphenol (sponsored)	Surface active agents	M/s Surfactants (P) Ltd. 28, Apollo Street, Bombay-1 (1969).	Exclusive. Industrial licence granted to the firm. Plant under fabrication.
19.	Opium alkaloids	Pharmaceuticals	Govt. of India, Ministry of Finance, New Delhi (1966).	Exclusive. Capacity planned 4. 7 TPA-value Rs. 1 crore. Fabrication of plant and civil engineering construction under progress.
20.	*p*-Menthane hydroperoxide	Synthetic rubber	M/s Camphor & Allied Products, Bareilly (1960).	Exclusive.

1	2	3	4	5
21.	Pentachlorophenol and other chlorophenolic compounds (sponsored)	Fungicides	M/s Bombay Chemicals (P) Ltd., Bombay-1 (1969).	Exclusive.
22.	Potentiometric strip chart recorder	Recording instruments	M/s Associated Instruments Manufacturers (India) Pvt. Ltd., New Delhi (1970).	Non-exclusive.
23.	Quinacridone pigment (sponsored)	Dye intermediate	M/s Lona Industries (P) Ltd., Dist. Kolaba (1970).	Exclusive.
24.	Sulphacetamide and its sodium salt (sponsored)	Pharmaceuticals	M/s Indian Schering Ltd., Bombay-1 (1969).	Exclusive.
25.	tert-Butylcatechol	Synthetic rubber	M/s Percynic Chemicals, Bombay-1 (1970).	Non-exclusive. Plant installation in progress.
26.	Terpene G (sponsored)	Perfumery, Insecticides	M/s Camphor & Allied Products, Bareilly (1968).	Exclusive.
27.	Vat Golden Yellow G. K. (sponsored)	Dye intermediate	M/s Amar Dye-Chem Ltd., P. B. 6471, Bombay-16 (1967).	Exclusive.
28.	Vitamin C	Pharmaceuticals	M/s Hindustan Antibiotics Ltd., Pimpri, Poona (1966).	Non-exclusive.Capacity 125TPA. Civil construction of the plant building in progress. Most of the plant has been ordered.

TABLE II (B)

Following processes which have been mentioned in Table I are also licensed on non-exclusive basis to the following additional firms and are awaiting production·

	Name of the process		*Name of the party & year of release*
1.	Dihydroisojasmone		M/s Sonebon Laboratories, Kottayam-5 (1970).
2.	DDT-water dispersible		M/s Pesticides Ltd., 28 Sayani Road, Bombay-28 (1967).
3.	Liquid rubber		M/s Swastik Rubber Products Ltd., Poona-3 (1962).
4.	Nicotine sulphate	(i)	M/s M. M. Patel, P. O. Sunav, Gujarat (1966).
		(ii)	M/s National Tobacco Bye-products, Dal Mandi, Saharanpur (1963).
		(iii)	M/s Tobacco By-Products P. Ltd., Fort Narsarawpet, Guntur (1963).
		(iv)	M/s Coromandal Tobacco Bye-Products, P.O. Gannavaram, Andhra Pradesh.
5.	Peach aldehyde		M/s Sonebon Laboratories, Kottayam-5 (1970).
6.	Polyurethane printing rollers		M/s United Ink & Varnish Co., P. B. 6862, Vile Parle, Bombay-57 (1965).
7.	Rubber base contact adhesive		M/s Bhagsons Paint Industries, 16-A DLF, Industrial Area, New Delhi-15 (1967).
8.	Sisal wax	(i)	M/s Shalimar Rope Works, 14, Netaji Subhash Road, Calcutta (1966).
		(ii)	M/s Deccan Paint & Chemical Industries, 298, G. T. Road, North Culcutta (1968).
		(iii)	M/s Industrial & Engg. Corp., 84-B, Bondel Road, Calcutta (1966).

TABLE II (Contd.)

9.	Styrene DVB-cation exchange resin	(i)	M/s Tulsi Industries, Poona-13 (1963).
		(ii)	M/s Bird & Co., Ltd., Chartered Bank Bldg. Calcutta-1 (1963).
10.	Thermistors		M/s Adept Laboratories, Poona-4 (1963).

A-XI TABLE III : PROCESSES APPROVED FOR RELEASE TO INDUSTRY BY 'PROCESS RELEASE COMMITTEE, N C L'

(T = Metric tonnes)

S. No.	Name of the process and Indian Patent No.	Field of utilization	Scale of development	Production envisaged per year	Expected annual turnover Rs. in lakhs	Remarks
1	2	3	4	5	6	7
1.	Aniline	Industrial chemicals	5 kg./hr.	600 T	18·00	—
2.	Atrazine	Herbicides	Lab. scale	50 T	17·50	Negotiations in progress.
3.	Butyl titanate	Varnishes & enamels	10 kg./batch	20 T	4·70	Agreement in progress.
4.	Cadmium sulphide photo-conductive cells	Electronic instruments	Lab. scale	30,000 cells	7·50	Released to two parties; one in production.
5.	Carbazole dioxazine violet pigment base	Organic pigment	1 kg /batch	10 T	30·00	—
6.	Catechol	Pharmaceuticals	Lab. scale	45 T	8·10	Released; awaiting production.
7.	Chlorobenzenes					
	(i) MCB	Industrial chemicals	0·25 T/day	3,500 T	101·50	—
	(ii) ODCB			300 T	9·96	
	(iii) PDCB			600 T	25·98	

1	2	3	4	5	6	7
8.	Chloromethanes					
	(i) Carbon tetrachloride	Industrial solvents	2·5 kg/hr.	228 T	5·93	Released; 300 TPA semi-commercial plant commissioned at the works.
	(ii) Perchloroethylene			30 T	1·05	
	(iii) Chloroform			15 T	0·88	
9.	Coating for oil filter paper	Paper	6 kg./batch	1,700 kg.	0·27	Released.
10.	Costus root oil	Perfumery	1 kg./batch	300 kg.	4·80	—
11.	Dimethylaniline	Industrial chemicals	9 kg./batch	600 T	36·90	Negotiations in progress
12.	Disperse dyes (116453)	Dyes	Lab. scale	—	—	Negotiations in progress.
13.	Ferric oxide (calcined & precipitated)	Catalyst	Lab. scale	1,100 kg.	0·44	—
14.	Fine Chemicals	Research	Lab./bench scale	—	10·00	Negotiations in progress.
15.	Double boiled linseed oil substitute	Foundry	100 kg./batch	1,200 T	24·00	—
16.	Fructose and chamazulene (108413, 108414)	Pharmaceuticals, Cosmetics	Lab. scale	3 T	1·80	—

1	2	3	4	5	6	7
17	Gaskets from coir pith	Gaskets	18″ × 18″ × ⅛″	5·32 T	1·27	—
18.	Glyceryl guaiacolate	Pharmaceuticals	Lab. scale	2 T	1·60	—
19.	*p*-Menthane hydroperoxide	Synthetic rubber	5 kg./batch	70 T	11·76	Exclusive. Released; awaiting production.
20.	Monochloroacetic acid	Weedicides, CMC	40 kg /batch	600 T	37·50	Negotiations in progress.
21.	*p*-Nitrophenol	Insecticides	40 kg./batch	300 T	39·75	Being released to HOC Ltd., Rasayani.
22.	Optical whitening agent for synthetic fibres	Textiles	Lab. scale	5 T	5·40	—
23.	Orthotolyl biguanide	Soap	50 kg./batch	5 T	1·25	Exclusive. Released; in production.
24.	Phenacetin	Pharmaceuticals	50 kg /batch	100 T	40·00	—
25.	Phenoxyacetic acid	Pharmaceuticals	50 kg./batch	20 T	3·64	—
26	Phenylacetic acid	Pharmaceuticals	1 kg./batch	60 T	13·08	—
27.	Phthalates					
	(i) Dioctyl	Plasticizers	60 kg./batch	5000 T	400·00	DOP in production.
	(ii) Dibutyl		25 kg /batch			—

1	2	3	4	5	6	7
	(iii) **Butyloctyl phthalate**	Plasticizers	25 kg./batch	1500 T	120·00	—
28.	Polyurethane coatings	Protective coatings	Lab. scale	25 T	3·75	Negotiations in progress.
29.	Potassium ethyl/amyl xanthate	Mineral beneficiation	Lab scale	300 T	24·00	—
30.	Potentiometric strip chart recorder	Recording instrument	—	1,200 units	90·00	Released; awaiting production.
31.	Recovery of pyridine bases (113111)	Dyestuffs	Lab. scale	—	—	—
32.	Rubber blowing agent	Rubber chemicals	10 kg /batch	30 T	4·05	In production.
33.	Rubber reclaiming agent	Rubber chemicals	20 kg /batch	100 T	10·00	In production.
34.	Rubberized cork sheets from cork waste	Gaskets	6″ × 9″ × 1/8″	5·32 T	1·27	—
35.	Hot and cold sachets	Domestic	20 × 10 cm.	1,00,000 sachets	1·50	Being released;.
36.	Sealants for canvas bags	Adhesives	5 kg /batch	500 kg.	0·20	—

1	2	3	4	5	6	7
37.	Simazine	Herbicides	Lab. scale	50 T	17·50	Negotiations in progress.
38.	Sorbitol—70% from dextrose monohydrate	Pharmaceuticals, Humectant	90 kg./batch	500 T	27·50	—
39.	(i) Sorbitol—70% from cane sugar	Pharmaceuticals Humectant	5 kg. sugar/ batch	350 T	19·25	—
	(ii) Mannitol from cane sugar	Pharmaceuticals	5 kg. sugar/ batch	46 T	11·50	—
40.	Staple pins adhesive	Stationery	10 kg./batch	5 T	1·00	—
41.	Terpineol	Perfumery	Lab. scale	100 T	22·00	—
42.	tert-Butylcatechol	Synthetic rubber	10 kg./batch	25 T	8·00	Released; awaiting production.
43.	(i) Theophylline & Aminophylline	Pharmaceuticals	Lab. scale	30 T	28·00	—
	(ii) Caffeine	—do—	—do—	30 T	18·00	—
44.	Vitamin B_6	Pharmaceuticals	Lab. scale	10 T	42·50	Negotiations in progress.

A–XII TABLE IV : KNOW-HOW AVAILABLE

(A) Know-how is available on various products/processes which are listed under Table III. These 44 processes are authorized for release by the Process Release Committee.

(B) In addition, know-how is also available on the following products/processes.

S. No. 1	Product/Process 2	Field of utilization 3	Scale of development 4	Remarks 5
1.	Anion exchange resin from melamine	Demineralization of liquids	Lab. scale	Non-exclusive.
2.	Antipriming composition	Antipriming in locomotives	Lab. scale	Non-exclusive ; already in production.
3.	BON acid	Dyestuff	3 kg./batch	
4.	Civetone & dihydrocivetone	Perfumery	Lab. scale	—
5.	DDT-water dispersible	Insecticides	15 kg./batch.	Non-exclusive ; licensed to 3 parties ; one in production.
6.	Dihydroambrettolide & Isoambrettolide	Perfumery	Lab. scale	—
7.	Dihydroisojasmone	Perfumery	Lab. scale	Non-exclusive; licensed to 2 parties; one firm in production.
8.	Dinitromonomethylaniline	Explosives	50 kg./batch	

1	2	3	4	5
9.	*dl*-Menthol from citronellal	Perfumery	Lab. scale	—
10.	Ethylene dichloride	Industrial solvent	3 kg./hour	—
11.	Exaltolide	Perfumery	Lab. scale	—
12.	Exaltone	Perfumery	Lab. scale	—
13.	Ferrites (Hard)	Electronics	Lab. scale	Non-exclusive; licensed to one firm; trial production started.
14.	Ferrites (Soft)	Electronics	Lab. scale	—
15.	Heat sealable coating composition	Achesives	Lab. scale	Non-exclusive.
16.	Hexachloroethane	Smoke screens, Foundry industy	10 kg./hour	Non-exclusive; being released.
17.	β-Ionone	Perfumery	5 kg./batch	Non-exclusive licensed to two firms; one in production.
18.	Liquid rubber	Adhesives, Rubber rollers	Lab. scale	Non-exclusive; licensed to two firms; one in production.
19.	Modified sugarcane wax	Polishing compositions	5 kg.batch	—
20.	Monoethylaniline	Explosives	10 kg./hour	—

1	2	3	4	5
21.	Neolavandulol	Perfumery	Lab. scale	—
22.	Nicotine sulphate	Insecticides	25 kg. of raw material/batch	Non-exclusive on zonal basis; licensed to five firms; one firm in production.
23.	Peach aldehyde	Perfumery	Lab. scale	Non-exclusive; licensed to two firms; one in production.
24.	Phthalates			
	(i) diethyl	Plasticizers	22 kg./batch	Non-exclusive; licensed to one firm ; in production.
	(ii) dimethyl		30 kg./batch	
25.	Polyurethane printing rollers	Printing	Lab. scale	Non-exclusive; licensed to three firms; one in experimental production
26.	Rubber base contact adhesive	Adhesives	Lab. scale	Non-exclusive; licensed to two firms;. one in production.
27.	Sisal wax 70%	Cosmetics, Polishes	3 kg./batch	Non-exclusive; licensed to four firms; one in production.
28.	Sorbitol	Pharmaceuticals	10 kg./batch	—
29.	Styrene DVB anion exchange resin	Demineralization of liquids	15 kg./batch	—
30.	Thermistors	Electronics	100 pieces/batch	Non-exclusive; released to three firms as technical aid; two in production.

A-XIII STAFF STRENGTH (1970-71)

1. Scientific	278
2. Technical	205
3. Non-technical	103
4. Class IV technical	138
5. Class IV non-technical	68
Total	792
6. Research workers	
a) JRF and SRF	47
b) CSIR Pool Officers	6
c) Guest workers	23
Total	76
7. Scientific staff working on sponsored projects	
a) NCL Staff	12
b) Staff from sponsors	9
Total	21

A-XIV COST-BENEFIT ANALYSIS FOR 1970-71

ACTUAL EXPENDITURE	Rs. in lakhs.
1. *Recurring expenditure*	
(a) Pay & allowances	44·20
(b) Chemicals & apparatus	12·26
(c) Maintenance & contingencies	6·89
Total (1)	63·35
2. *Capital expenditure*	
(a) Building	0·52
(b) Equipment & apparatus	4·30
(c) Services & miscellaneous	3·81
Total (2)	8·63
3. *Pilot plant expenditure*	
(a) Pay and allowances	2·41
(b) Raw materials and miscellaneous	1·10
(c) Equipment, buildings and services	0·26
Total (3)	3·77
Total CSIR expenditure (1+2+3)	75·75
4. *Expenditure on account of sponsored projects*	6·68
Total	82·43

BENEFITS

Receipts

1. Premia and royalties	1·06
2. Receipts on account of sponsored projects	6·68

3.	Analytical and testing charges, technical aid etc.	0·65
4.	Institutional consultancy (CSIR share)	0·19
5.	FCP (Fine Chemicals Project) Sales	2·46
6.	Miscellaneous receipts	3·97
	Total	15·01

Indirect benefits

1.	Total number of processes in production	55
2.	Value of production based on NCL know-how during 1970-71 (Rs. in lakhs)	283·84
3.	Estimated saving in foreign exchange on account of above production (Rs. in lakhs)	113·54
4.	Total cumulative value of production upto March 1971 (Rs. in lakhs)	576·81
5.	Research papers published during 1970-71	91
6.	Doctorate and Masters degrees awarded during 1970-71	7
7.	No. of recognized guides for Doctorate and Masters degrees	38
8.	Patents	
	(a) New patents filed	7
	(b) Total patents in force	37
	(c) Patents which are being commercially exploited.	22
9.	Total number of technical enquiries on which information was supplied.	2135

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