

ANNUAL REPORT 1966-67



NATIONAL CHEMICAL LABORATORY
POONA

NATIONAL CHEMICAL LABORATORY
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COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

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INTRODUCTION

The present Report covers the period April 1966 to March 1967. It may be noted that sixty-one product-oriented research schemes have been reviewed in a separate chapter of the Report.

Twenty-six processes developed by the Laboratory are in production; eighteen more have been released to industries, and are awaiting production. Thirty-seven processes, for which details have been obtained, are under evaluation. The present status of these processes is described in the Appendices XI, XII and XIII of the Report.

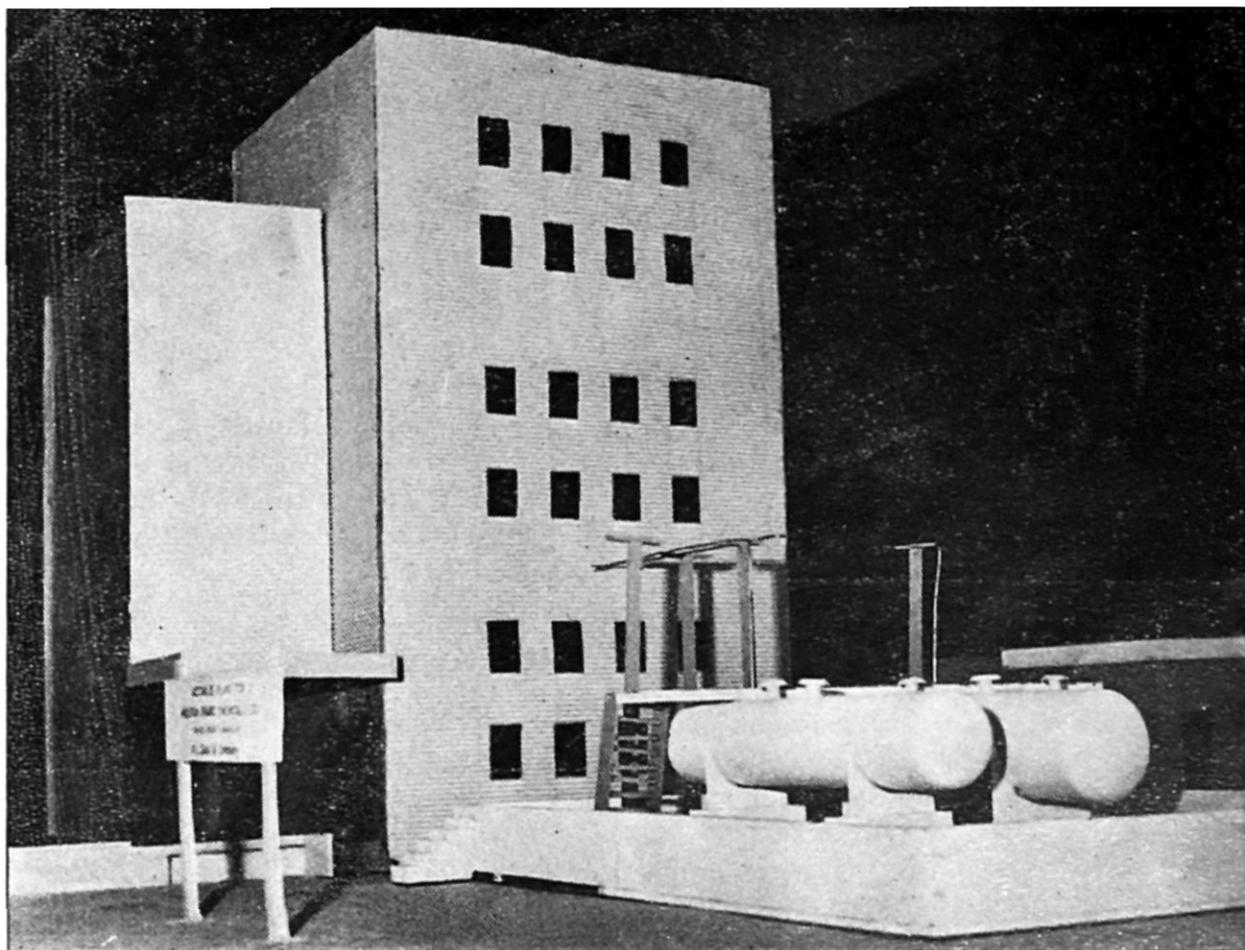
During the year under review, work on twenty-one sponsored schemes from private industries, six from Government agencies and four PL-480 schemes was in progress. Their respective financial contributions were Rs. 4.31, 2.32 and 4.52 lakhs, as against the recurring expenditure of Rs. 49.7 lakhs of the Laboratory. The sponsored work on the liquid phase catalytic oxidation of toluene to benzoic acid was completed, and a 500 TPA plant is under erection at Bombay. M/s. Travancore Titanium Products Ltd., Trivandrum, who had sponsored work on the production of titanium tetrachloride from ilmenite, are well ahead in the erection of a 500 kg/day titanium tetrachloride plant based on the NCL designs.

Seven pilot plant projects were in progress during the year under review. Work on dimethyl and diethyl phthalates was successfully completed and the know-how has now been sold to industry. The turn-key offer for 2000 TPA acetanilide plant based on the NCL know-how has now been selected by M/s Hindustan Organic Chemicals Ltd., Rasayani, from among world tenders invited. Installation of a new factory at Neemuch by the Ministry of Finance, which will manufacture semi-refined morphine and other alkaloids from Indian opium based on the NCL know-how, is in progress. M/s. Hindustan Antibiotics Ltd., Pimpri, are going ahead with plant designs for the erection of a 125 TPA vitamin C plant based on the NCL know-how. M/s. Chemaux Pvt. Ltd., Bombay, have installed the plant to produce 9 tonnes of bacterial diastase per year, based on the NCL know-how and the plant is being put into commission. The design and fabrication of a proto-type vapour phase chromatograph with thermal conductivity type detector has been completed, and work on other detectors is in progress.

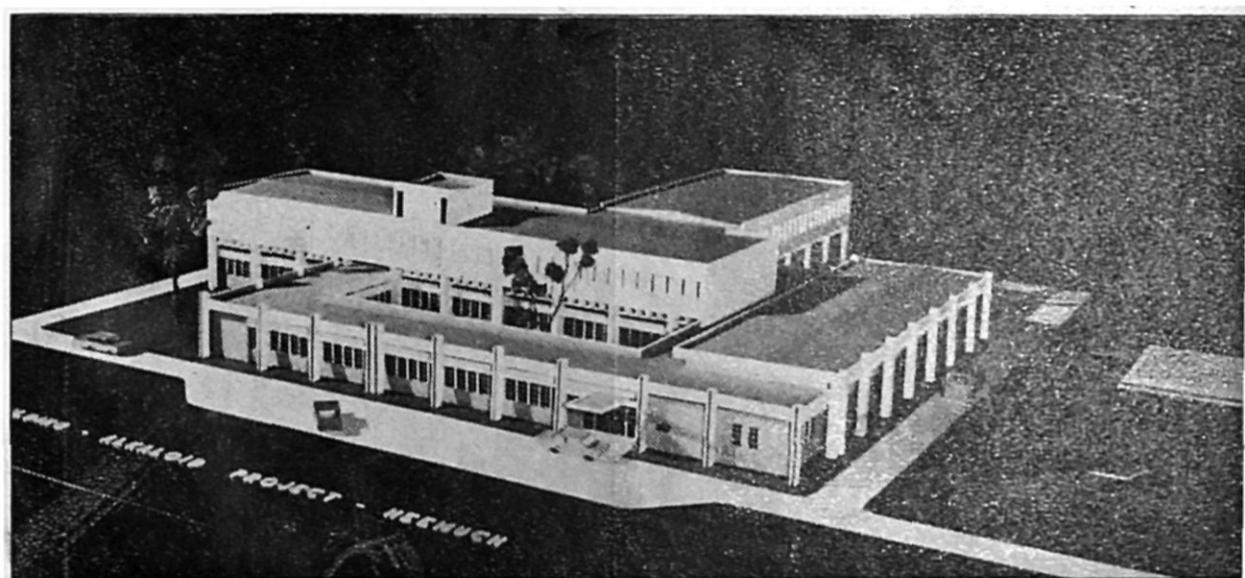
The money value of the chemicals and instrument referred to above, which are expected to be produced commercially within the next two years, is estimated to be about Rs. 5 crores.

The Laboratory has also maintained its excellent record of basic research. Thus, 130 papers were published and 18 read at various symposia. 20 Patents were filed, bringing the total number of patents in force to 81.

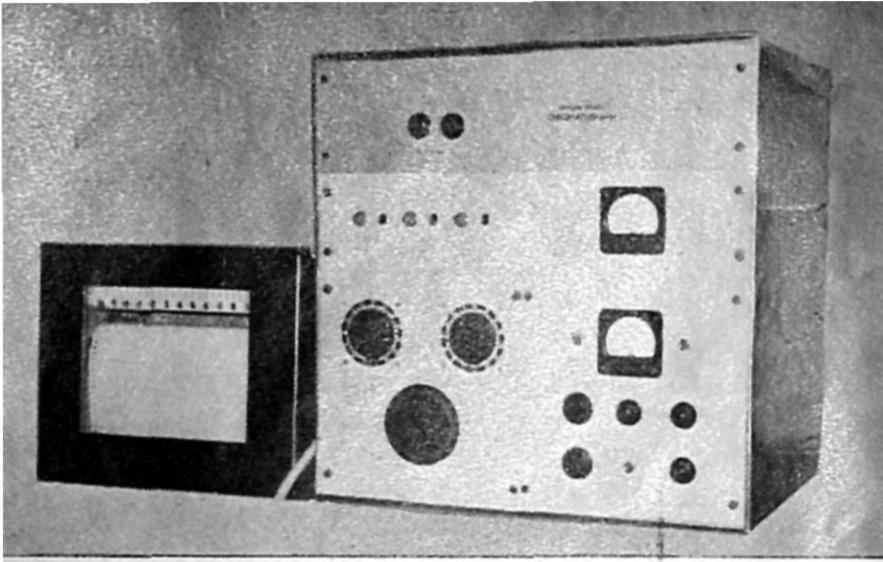
A brief résumé of the highlights of the research projects in progress is given in the Report.



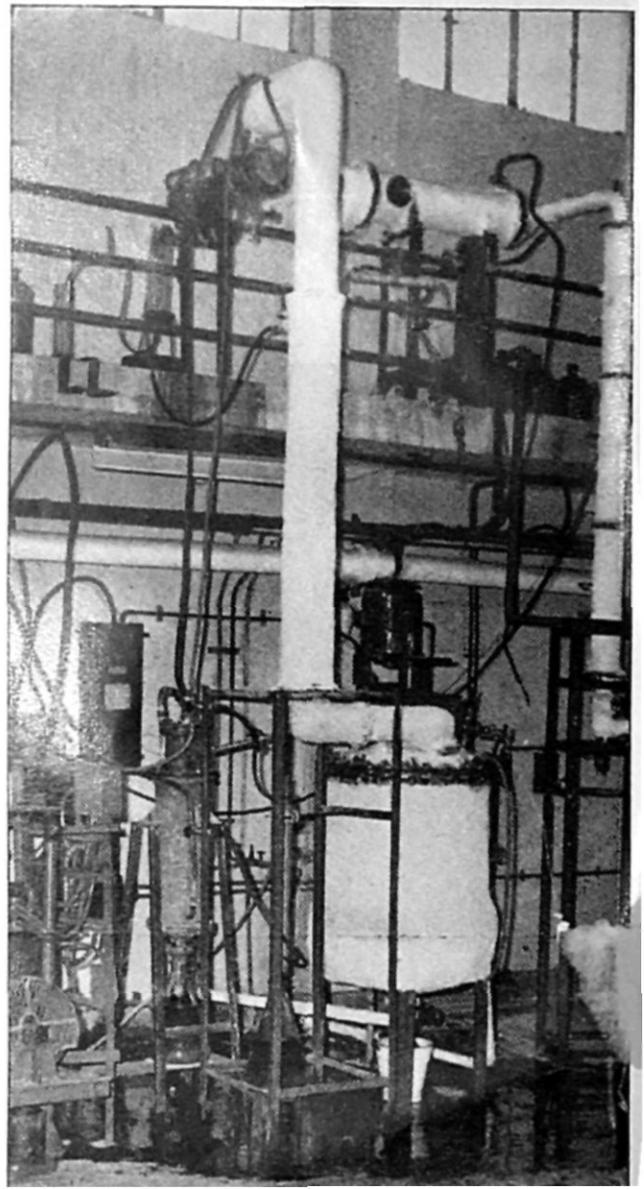
Model of the Acetanilide plant to be erected at HOC Rasayani, Maharashtra. (Page 150, item 1).



Model of the Opium factory under erection at Neemuch M. P. (page 151, item 8).



Proto-type Vapour Phase Chromatograph unit (page 159, item 36).



NCL pilot plant set up to produce 100 Kg. Acetanilide / batch.

SPONSORED PROJECTS

PRIVATE PARTIES

INTERMEDIATES

1. *Benzoic acid*

The scheme has been undertaken to follow up the preliminary laboratory-scale experiments carried out by the sponsor and to optimize the operating conditions for the liquid phase catalytic oxidation of toluene to benzoic acid.

The conditions of temperature, pressure, catalyst concentration and time of reaction were first standardized on a 2-litre capacity unit. On successful operation of this small unit, a 10kg/hour pilot plant was installed, run continuously for several days, and the product sent to the sponsor. It was observed that the same pilot plant could be operated at twice the capacity with certain modifications. Appropriate modifications have been suggested in the existing pilot plant to enable it to operate at over 20 kg/hour. The entire plant will be shifted to the sponsor's factory where, with the suggested modifications, it can be operated to produce about 150 T/annum of benzoic acid.

2. *Industrial chemicals from diketene*

Ketene is a versatile key intermediate for the manufacture of a variety of industrial chemicals such as acetic anhydride and other acetyl derivatives, cyclic lactones (propiolactone for making acrylic acid) and crotonaldehyde from which sorbic acid can be prepared. Ketene can be dimerized to diketene which is easily converted to pyrazolones, acetoacetic esters, acetoacetanilide, and other acetoacetarilides such as Naphthol AS-G.

The annual requirement of diketene in India for preparation of above intermediates is estimated at 200-300 T/annum. Because of the instability of ketene and diketene, they are not imported.

Work on this project is divided into the following steps:

- (i) Acetic acid $\xrightarrow{\text{dehydration}}$ ketene
- (ii) Ketene $\xrightarrow{\text{dimerization}}$ diketene
- (iii) Diketene \rightarrow industrial chemicals mentioned above

The major raw material, acetic acid, is available in the country. At present two ketene furnaces of imported origin are in operation in the country and ketene so produced is employed for the manufacture of acetic anhydride for captive consumption.

Experimental conditions for the dehydration of acetic acid to ketene have been standardized on a laboratory scale and good conversion efficiency has been established in a specially constructed furnace. The conversion is being optimized in a bigger furnace to obtain a steady source of ketene for the dimerization step.

3. *Nonylphenol*

Nonylphenol is used in the preparation of ethylene oxide condensates used as non-ionic surfactants. It is also used for the preparation of anionic surfactants, additives and antioxidants for lubricating oils. Nonylphenol is finding increasing applications in the preparation of protective coatings, plasticizers and solvents, etc. At present nonylphenol is not manufactured in India.

Nonylphenol was prepared by condensation of phenol and propylene trimer. Different catalysts were tried to optimize yields. Excellent yields of nonylphenol were obtained on laboratory scale, as well as on a pilot plant scale. Complete process data have been submitted to the sponsor.

DYES

4. *Anthraquinonoid intermediates and dyes*

These are industrially important. The object is to study spectroscopic and chromatographic methods for the analysis of anthraquinonoid intermediates and dyes and determination of the structures of some commercial dyes.

Chromatographic and spectroscopic methods of analysis have been developed for a few anthraquinonoid intermediates for vat, acid and reactive dyes.

5. *Chlorinated copper phthalocyanine*

This is a bright green pigment possessing excellent tinctorial and fastness properties, and is widely used in paints, plastics, and printing inks.

The chlorination conditions, to produce a material of the desired shade and fastness properties, are being established. A few runs on 0.5 kg. (final

product) per batch scale were carried out by the conventional process in a glass reactor. The shades obtained were not completely satisfactory, so the procedure is being re-examined.

An entirely new process involving less tedious operations for the chlorination is also being investigated simultaneously.

TERPENOIDS

6. *Improvements in the process for the manufacture of l-menthol from dementholised peppermint oil*

The sponsor is producing *l*-menthol from imported dementholized peppermint oil. The present work was undertaken to simplify the process followed by the sponsor, and to improve the overall yield of the final product. A stereospecific method of reduction of *l*-menthone to *l*-menthol and a convenient method to separate *l*-menthol from the mixture of menthol isomers have been standardized and recommended to the sponsor. Systematic investigation has established that the maximum yield of *l*-menthol from dementholized peppermint oil depends upon the following factors: (1) conversion of menthyl acetate to menthol, (2) efficient fractionation of the dementholized peppermint oil to achieve the separation of *l*-menthol by natural cycle (3) suitable method of reduction for conversion of menthone to menthol, preferentially stereospecific in nature, and (4) the method to separate *l*-menthol from the mixture of menthol isomers formed during reduction. All these processes have been demonstrated to the representative of the firm. The sponsor has accepted the modifications suggested and accordingly these are being implemented by the firm.

7. *Utilization of longifolene and Δ^3 -carene*

The Indian turpentine oil (*ex-Pinus longifolia*) contains large quantities of longifolene and Δ^3 -carene. The pinenes are present only to the extent of nearly 20%. In the foreign turpentine oils the pinene content is upto 95% and hence almost all uses of these oils are based on the chemistry of pinene. In order to utilize the Indian turpentine oil having lesser contents of pinene as a raw material for industrial products, it is imperative that suitable outlets must be found for the utilization of longifolene and Δ^3 -carene.

The scheme has been undertaken to find suitable industrial outlets utilizing longifolene and Δ^3 -carene.

A number of products from longifolene were prepared and sent to the sponsor for evaluation. The sponsor is likely to undertake the preparation of one of these products on commercial scale.

A number of reactions of Δ^3 -carene were investigated and several products sent to the sponsor for evaluation. One of them approved by the firm was prepared on a larger scale. The firm is likely to go into production of this item.

8. *Utilization of terpene-G*

Terpene-G is a by-product in the manufacture of camphor from turpentine oil. Work has been undertaken to prepare useful products from this component.

Chlorinated product of camphene, known as Toxaphene, is a good insecticide. Terpene-G, which consists of mostly dihydrocamphene and camphene, was therefore chlorinated and a large sample was supplied for evaluation.

AGRICULTURAL CHEMICALS

9. *Aminotriazole*

Aminotriazole is a useful herbicide having a potential market in the country. Work has been undertaken to develop an economical process for the manufacture of aminoguanidine and aminotriazole. Aminoguanidine is the penultimate intermediate in the manufacture of aminotriazole.

A literature survey of the methods available for the production of aminotriazole starting from a basic raw material such as calcium cyanamide was made. Nitroguanidine is in production at present by the Defence Department, from whom a small quantity was obtained for our experiments. Attempts were made to prepare aminoguanidine by electrolytic reduction of nitroguanidine in which 50% yield could be obtained. Aminoguanidine can further be converted to aminotriazole in practically quantitative yields by a known method.

It is further gathered that the work on electrolytic conversion of nitroguanidine to aminoguanidine has already been carried out in CECRI Karaikudi. In view of this the sponsored work is temporarily suspended.

DRUGS AND PHARMACEUTICALS

10. *Calcium hypophosphite*

Calcium hypophosphite is used in pharmaceutical industry and is a constituent of many general tonic preparations. At present it is not made in the country and is imported to the tune of 50 T/annum valued at Rs. 5 lakhs.

Work has been undertaken to develop a process for the production of calcium hypophosphite from lime and imported yellow phosphorus. A unit for 30 kg/batch of calcium hypophosphite will be designed for the sponsor.

The reaction conditions to treat 1 kg. of phosphorus per batch have been standardized and improvements on the recovery of the by-product phosphoric acid are being worked out by introducing modifications in the P_2O_5 absorption and phosphine delivery systems. The absorption step was studied in detail and 50-60% of the expected recovery of phosphoric acid has been achieved.

11. *Carbimazole*

Carbimazole, a drug used in the treatment of hyperthyroidism and angina pectoris, is considerably less toxic than most drugs used for the same purpose. An optimum process for the synthesis of carbimazole has been standardized to produce 300 g. batches of the material. The product conforms to the B. P. specifications in all respects.

12. *Investigation of a fermentation problem*

During storage of some of the Ayurvedic pharmaceutical preparations (such as Asavas and Arishtas), it was observed by the sponsor that there was some spoilage of the final products for reasons not easily detectable in their manufacturing processes. The present work has been initiated to investigate the causes of the above mentioned spoilage, and to suggest remedial measures for the same.

Possible causes of spoilage of the preparations marketed by the firm were examined, and the contaminating organisms were studied in detail. Methods for destroying and/or preventing the growth of the spoilage organisms were studied.

13. *Isolation of emetine from ipecac roots*

The principal therapeutic use of emetine is in the treatment of amoebiasis. At present large quantities of emetine are imported and consumed by the Indian pharmaceutical industry. It is known that large scale cultivation of ipecac plants is in progress in the districts of Nilgiris and Darjeeling. Laboratory scale extraction experiments on the imported and Indian varieties of ipecac roots were carried out, and conditions for the isolation of emetine have been optimized. Along with emetine, cephaeline was also obtained.

Conditions for the conversion of cephaeline to emetine have also been worked out.

14. *Radio-opaque dyes (like 'Urografin' and 'Biligrafin')*

Radio-opaque dyes are of great importance in X-ray diagnostic studies. At present these are not manufactured in India and the total requirements are met by imports. Work has been undertaken to develop know-how for some of these preparations.

Starting from 3,5-diaminobenzoic acid, optimum conditions of the steps on iodination, acetylation and the preparation of the sodium salt of diatrizoic acid were established. The latter is the main constituent of 'Urografin'.

Methods to prepare intermediates required in the synthesis of iodipamide, viz., iodine monochloride, adipyl chloride and 2,4,6-tri-iodo-*m*-aminobenzoic acid, have been standardized. The process for the purification of 2,4,6-tri-iodo-*m*-aminobenzoic acid has been modified and improved yields have been obtained. Iodipamide is the main constituent of 'Biligrafin'.

15. *Sodium cyclamates*

The chemical is fifty times as sweet as sucrose and is used as a non-nutrient sweetening agent in different types of food and beverage preparations.

Optimum conditions have been standardized on 250 g/batch scale, of the final product. Further experiments on large scale preparations of the product will be conducted at the sponsor's factory.

16. *Sorbide nitrate*

Iso-sorbide dinitrate, a coronary vasodilator, is used in the treatment of angina pectoris. It is effective in lowering blood pressure in hypertensives. Conditions for the technical preparation of the final product have been established on 1.5 kg/batch scale, based entirely on indigenously available raw materials. All the steps in the preparation have been finalised and a complete report of the work has been submitted to the sponsor. The firm is establishing a manufacturing unit for this chemical based on the results obtained.

17. *Sulphacetamide and its sodium salt*

In the form of a solution or ointment, sulphacetamide sodium is mainly used to treat eye infections. Using suphanilamide as starting material, conditions for the preparation of sulphacetamide and its sodium salt have

been standardized on 3 kg/batch scale, of final product. Attempts are also being made to purify the locally available material to meet the sponsor's specifications.

18. *Vanillin and ethylvanillin*

Vanillin is a popular flavouring agent for different food preparations. It is manufactured either from lignosulphonic acid present in sulphite liquor, which is available as a by-product of paper mills, or starting from *o*-anisidine. In India, few paper factories follow the sulphite process. At present vanillin and ethylvanillin are not manufactured in the country. The quantity and value of their imports are: vanillin 23 T/annum, value Rs. 10 lakhs; ethylvanillin 5 T/annum, value Rs. 3 lakhs.

Vanillin and ethylvanillin can be synthesized starting from *o*-anisidine and *o*-phenetidine respectively. Although these dyestuff intermediates are at present imported, they are on the manufacturing programme of a leading dyestuff factory and are likely to be available indigenously.

In the first instance, technical preparation of vanillin from *o*-anisidine through guaiacol is being studied on a laboratory scale. The first step consists of conversion of *o*-anisidine to guaiacol through the diazotisation reaction. Based on anisidine, more than 80% yields of guaiacol have been obtained. Starting from guaiacol, vanillin is prepared by condensation with formaldehyde and simultaneous reaction with nitrobenzene sulphonic acid and aluminium powder. Experiments are being carried out to optimize the yields of vanillin in the above reactions.

Similar studies will be conducted for the preparation of ethylvanillin starting from *o*-phenetidine.

CATALYSTS AND INDUSTRIAL INORGANIC CHEMICALS

19. *BD-catalyst*

Sponsored work has been undertaken to develop a method for the preparation of the catalyst used in the manufacture of butadiene from ethanol and acetaldehyde. The physico-chemical properties of the samples prepared will be tested in the laboratory and activity trials will be taken by the sponsor.

20. *Calcium silicate*

The sponsor has been manufacturing Thermolite insulating blocks, but the density of Thermolite prepared by the firm is somewhat high and this

is primarily due to the density of the calcium silicate used. Thus first phase of this investigation was to obtain calcium silicate of low bulk density. Samples of calcium silicate having bulk density of 8-12 lbs./cft. and other characteristic properties were prepared from indigenous raw materials and several insulating blocks of low density were moulded. Properties of the insulating materials are now under examination. Preliminary experiments have given encouraging results.

PULP AND CARBOHYDRATES

21. *Rayon grade pulp from some species of wood*

Under agreement with the sponsor, pulp is being made by different processes like prehydrolysis sulphate and sulphite from the species of woods supplied by the party. These pulps are tested for their filtrability and other properties so as to evaluate them for the manufacture of rayon yarn.

During the period, 4 species of woods have been investigated and the results communicated to the sponsor.

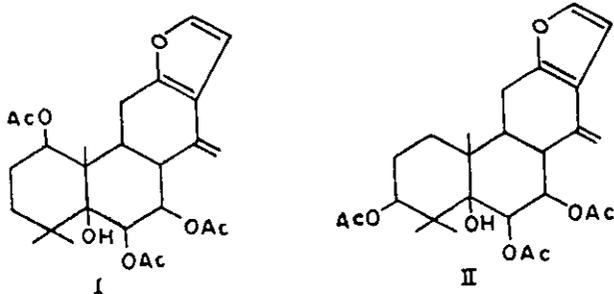
Large scale trials on the selected species of woods are in view.

CENTRAL AND STATE GOVERNMENT INSTITUTES

1. *Composite drug research scheme on Indian medicinal plants* (Ministry of Health, Govt. of India)

This work has been undertaken to study the chemistry of some of the Indian medicinal plants. The individual isolated components will be tested for their pharmacological properties by another unit organized elsewhere.

1.1 *Caesalpinia bounducella* Flem (*Putikaranja*) *Leguminosae* : The preliminary reports received from the Pharmacological Unit show that the various extracts are devoid of any useful activity. From the chloroform extract of the defatted seed kernels, seven closely related fatty acid esters of long chain alcohols and six closely related diterpenoids other than the reported caesalpins have been isolated. On the basis of spectral evidence two of the diterpenoid compounds E_3 (m.p. 122-23°) and E_4 (m.p. 253-54°) have been assigned the tentative structures I and II respectively.



1.2 *Asparagus Racemosus Willd (Shatavari) Liliaceae* : Pharmacological testing indicated three extracts (i. e. alcohol, ethyl acetate and acetone) to contain an active substance that blocks uterine activity, both spontaneous and induced by acetylcholine and oxytocin. In view of this, efforts were directed on the ethyl acetate and alcohol extract.

Ethyl acetate extract : The extract, which responds to saponins foam test, furnished on acid hydrolysis a mixture of steroidal saponogenins. This, on column chromatography (SiO_2/II), gave two pure crystalline saponogenins (A & B). Saponogenin A has been identified as sarsasapogenin.

Ethanol extract : This also responds to saponins foam test and has been separated into glycosidic and non-glycosidic portions. The glycosidic portion has been shown to possess the main pharmacological activity of the crude drug. The crude glycosidic preparation has been further segregated into two fractions consisting essentially of single glycosides. Pure samples have been sent for pharmacological evaluation.

1.3 *Boerhavia diffusa Linn (Punarnava) Nyctaginaceae* : As the Pharmacological Unit reported useful diuretic activity for the petroleum ether extract, and other extracts were pharmacologically un-interesting, efforts were mostly directed to the petroleum ether extract. It was separated into acidic and neutral fractions by aqueous alkali, and the fractions are being pharmacologically activated.

Another closely related species of *Boerhavia punarnava* has also been investigated and various extracts are being screened for the reputed medicinal properties of the plant.

2. *Commercial uses of Punjab costus roots - (Kuth)*
Saussurea lappa Clarke. (Govt. of Punjab)

The scheme envisages the assessment of the costus roots available in the region for different commercial uses.

A large number of samples of roots, grown under various manurial and irrigational trials and supplied by the Govt. of Punjab, have been examined for yield of oil and lactones and their physico-chemical properties determined. The results have been communicated to the sponsor.

Hexahydrocostunolide was prepared and sent to leading perfumery houses abroad for its perfumery evaluation. Though the reports are encouraging, the possibility of its commercial exploitation would depend largely upon its availability at a reasonable price, which again would depend on the size of the market for the oil. For every 200 g. of hexahydrocostunolide, about 2 kg. of costus root oil is also obtained during the process, and this has to find a ready market.

Conditions have been standardized for the extraction of costus root oil by *n*-hexane, a solvent which is indigenously available. The oil so obtained is also found acceptable to perfumery industry. On the basis of the work carried out it would be possible to establish a commercial unit for production of costus root oil. The work is now concluded.

3. *Fabrication of Electron Diffraction Camera*

The technical know-how for the fabrication of this costly equipment has been developed. One such unit is being used at present in NCL and two more are in actual use at Bhabha Atomic Research Centre, Bombay, and National Metallurgical Laboratory, Jamshedpur.

The project includes designing and fabrication of electron diffraction equipment and associated accessories; to assist outside parties in connection with installation of high tension unit, and training of personnel in this field.

Fabrication of the equipment has been undertaken for three more parties: (1) Gauhati University, Assam (2) Fertilizer Corporation of India, Sindri, and (3) Defence Science Laboratory, New Delhi. The unit for Gauhati University has been fabricated, and final testing is in progress.

4. *Constitution of lac*
(Indian Lac Research Institute, Ranchi)

Very little is known about the chemical constitution of the resin molecule of lac. The present study has been undertaken with a view to unravel

the structure of lac resin as this knowledge is a prerequisite for opening new fields of lac utilization.

A number of acids arising from the hydrolysis of lac, namely jalaric, shelloic, epishelloic, laksholic, epilaksholic, butolic and aleuritic have been isolated. The structures of jalaric, laksholic and epilaksholic were established for the first time. Results obtained strongly suggest that the chief building blocks of lac resin are aleuritic acid and jalaric acid. The isolation of the pure fraction of the resin using repeated precipitations has been successfully completed.

The pure resin thus obtained has been oxidized and hydrolysed, and the product so obtained has been characterized. This work has thrown significant light on the mode of linking of the building blocks of the lac resin. Work has been undertaken on selective hydrolysis of lac resin.

5. *Lac dye* (Indian Lac Cess Committee, Ranchi)

The colouring matter of lac is under investigation. There are possibilities of using lac dye in various fields. The object of the scheme is to find uses for the colouring matters of lac.

The complete structure of one laccaic acid containing nitrogen has been determined. Work on the isolation and characterization of non-nitrogen containing lac pigments has been undertaken.

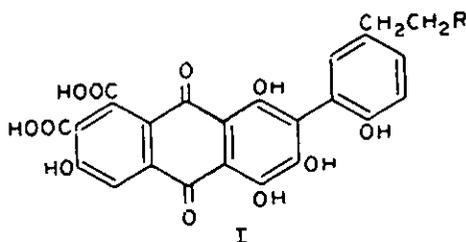
When the crude laccaic acid (the isolation of which was described in the earlier report) was dissolved in *n*-butanol saturated with 0.3 N hydrochloric acid and chromatographed on polycaprolactam powder using the same solvent system for development and elution, a minor fast moving fraction was collected, followed successively by two main fractions. Extraction of each with saturated aqueous sodium acetate and acidification with hydrochloric acid yielded laccaic acid A and B respectively. Laccaic acid A separated as bright red needles and could be recrystallized from water or methanol.

The constitution of laccaic acid A has now been proved to be (I); R=NHCOCH₃ (paper 64) mainly on the basis of NMR spectral data. The ether-esters were obtained by methylation with dimethylsulphate and potassium carbonate in acetone. Laccaic acid B is very closely related to laccaic acid A, the structure being (I); R=OH. It was originally considered that laccaic acid B may be an intramolecular or intermolecular carbonate of (I); R=OH,

but it has now been found that the group $\text{CH}_2\text{CH}_2\text{-O-COOME}$ present in some of the ether-esters of laccaic acid B and the corresponding xantholaccaic acid, are artefacts produced by the action of dimethylsulphate and potassium carbonate in acetone on the alcohol (I); $\text{R}=\text{OH}$. Conversions of laccaic acid A derivatives to laccaic acid B derivatives have been achieved.

Erythrolaccin is accompanied by another pigment in very small quantity and its structure has been shown to be 3,6,8-trihydroxy-1-methylantraquinone.

The synthesis of 2-phenylanthraquinone derivatives related to the laccaic acids is in progress.



6. *Titanium tetrachloride from ilmenite*
(M/s Travancore Titanium Products Ltd., Trivandrum)

The titanium dioxide white pigment is at present manufactured from Indian ilmenite by the sulphate process. The process yields titania of anatase grade and requires substantial quantities of imported sulphur in the form of sulphuric acid. To obtain rutile grade titania of commerce by the above process, rutile seed is prepared from titanium tetrachloride and employed during the hydrolysis of sulphate liquor. The amount of titanium tetrachloride required to be imported for this purpose is of the order of 50 T/annum, valued at Rs. 1.5 lakhs.

Work carried out earlier in this Laboratory on a small scale (2 kg. TiCl_4 /hour) was scaled up in the present scheme. The data thus obtained are being utilized for the installation of a plant at the sponsor's factory to produce titanium tetrachloride for captive consumption. The plant is likely to go on stream by the end of 1967.

The iron chloride by-product obtained in the beneficiation step of the process was successfully converted to the pigment grade iron oxide on a laboratory scale.

A laboratory-scale unit for burning titanium tetrachloride to the dioxide in an oxy-hydrocarbon flame has been set up and preliminary runs have been carried out.

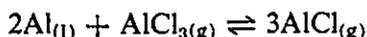
PL-480 SCHEMES

1. *Chemical and thermodynamic properties of refractory materials at high temperatures*

(National Bureau of Standards, Washington)

Thermodynamic properties of refractory materials (useful in ceramic industry, production of atomic energy etc.) at high temperatures are being studied, employing high temperature techniques such as transpiration, Langmuir free evaporation and Knudsen cell effusion.

The following equilibrium reactions were studied at temperatures 1125° to 1425° K (Paper 47).



The reaction of $\text{AlCl}_{(g)}$ and $\text{MgO}_{(c)}$ between 1298° K and 1465° K was found to yield a spinel of magnesium oxide and Al_2O_3 (Paper 50).



The reaction $\text{AlCl}_{(g)}$ with $\text{BeO}_{(s)}$ between 1150° to 1350° K was studied and was found to yield a spinel of BeO and Al_2O_3 together with gaseous product $\text{BeCl}_{(g)}$.

Light-lanthanone sesquisulphides (Pr_2S_3 , Nd_2S_3 and Sm_2S_3) were employed to purify nitrogen gas free from oxygen. The method is satisfactory for reducing the oxygen content to a partial pressure of 10^{-18} atm. by using Pr_2S_3 and to 10^{-19} atm. with Nd_2S_3 and Sm_2S_3 at about 500°C.

Crystalline aluminium oxychloride AlOCl , prepared by the reaction of Al_2O_3 with AlCl_3 at 320° in a sealed tube, was found to decompose at 450 to 500° under atmospheric conditions. The stability of the solid was found to increase in a carrier gas (nitrogen) saturated with $\text{AlCl}_{3(g)}$. No decomposition was observed even at 650°. At 700°, however, 80% of the oxychloride was decomposed. Chemical analysis of the product indicates that the decomposition may be expressed as :



To study the vaporization of the compounds like tungsten carbide and sulphides of rare earths by Knudsen effusion technique at about 2000°C, a vacuum microbalance has been fabricated. The balance will be mounted on a high temperature graphite resistor furnace.

2. *Work on investigations on the synthesis and properties of new type glycol monoalkyl ethers for the control of water evaporation to extend the industrial utilization of cotton seed oil*

(U. S. Department of Agriculture, Washington)

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

Pure C₁₆ to C₂₂ alkoxy ethanols have been synthesized by Williamson's method. The monolayer properties of alkoxy propanols of C₁₆ and C₁₈ alcohols have been investigated. In order to understand the effect of extending the polar group by one more CH₂ on water evaporation reduction, the monolayer properties of alkoxy ethanols and propanols are being compared.

The surface viscosity measurements of C₁₆ to C₂₂ alcohols have been completed at various temperatures and pressures. From the above study it has been found that a number of two dimensional phase changes exist in the temperature range of 15-30°. Surface viscosity measurements of alkoxy ethanols have been undertaken.

Different monolayer properties of odd and even chain alcohols have been studied for comparing their characteristic behaviours.

π -A isotherms of the odd chain alcohols (C₁₇-OH, C₁₉-OH) were found to lie in between those of the adjacent even chain ones. π -A isotherms of C₁₈-OH were studied for different pH of the substrate water and at different temperatures. The results indicate the expansion of the monolayer above pH 10 and no distinct variation was observed in the π -A isotherms between pH 2.5 to 9.

The collapse pressure increases from C₁₆-OH to C₁₈-OH whereas it decreases in the case of C₁₉-OH to C₂₂-OH. The equilibrium spreading pressures of C₁₇-OH and C₁₉-OH have been found higher than those of

C_{16} -OH and C_{18} -OH respectively, indicating the varying influence of the even and odd carbon chain.

Surface potential measurements have been undertaken with a view to understand the orientation of the molecules in monolayers at various film pressures. In case of C_{18} and C_{20} alcohol films the transition pressures obtained by surface potential measurements have been found to agree fairly well with those of the pressure area isotherms. On calculating the surface dipole moment for each film, it has been observed that the surface dipole moment decreases as surface potential increases.

It is known that these long chain fatty alcohols possess in their bulk state three phase modifications and it is expected that in one of these phases it may have maximum spreading properties. D.T.A. studies were carried out to understand the properties of the monolayers spread from bulk materials, for evaluating transition temperatures, bulk phase modifications and associated thermodynamic quantities.

It has been observed that in a temperature range 23° to the fusion temperature, all the compounds with the exception of C_{18} -OH exhibit two phase modifications.

Optical microscopic studies of these alcohols and alkoxy ethanols have been undertaken. These help in interpreting the associated structure changes in the bulk as well as in the monolayer phases.

Surface thermodynamic properties of lower homologues of alkoxy ethanols were measured to follow the interaction of the polar group with the water sub-phase. The measurements of surface tension, vapour pressure, and heat of mixing were carried out at different temperatures and concentrations.

3. *Investigation of the effect of heat on Tung oil and derivatives of Tung oil and the characterization and identification of compounds resulting from heat treatment to extend the utilization of Tung oil.*

(U.S. Department of Agriculture, Washington)

The investigation deals with the thermal treatment of tung oil and its derivatives with a view to extend the utilization of this drying oil by the development of new industrial chemicals.

Methanolysis of tung oil was found to be simple and convenient for the large scale preparation of methyl eleostearate. Mild thermal treatment of

methyl eleostearate, in presence of catalyst, resulted in a 30% conversion to the cyclic monomer. It was found that the monomer is formed *via* the initial isomerized triene with the 11-double bond *cis*-configured. Isolation of this unique isomer of eleostearate has been reported for the first time.

The structure of the 14.1 μ cyclic monomer (readily accessible by sulphur-catalyzed thermal cyclisation of methyl α -eleostearate) has been unequivocally proved to be methyl 5-butyl-1,3-cyclohexadiene-6-caprylate on the basis of spectral and incisive chemical evidence.

This work has been extended to the indigenously available Kamala seed oil.

4. *Wood phenolics with special reference to their use in chemotaxonomy and their biosynthesis by tissue culture studies*

(U. S. Department of Agriculture Washington)

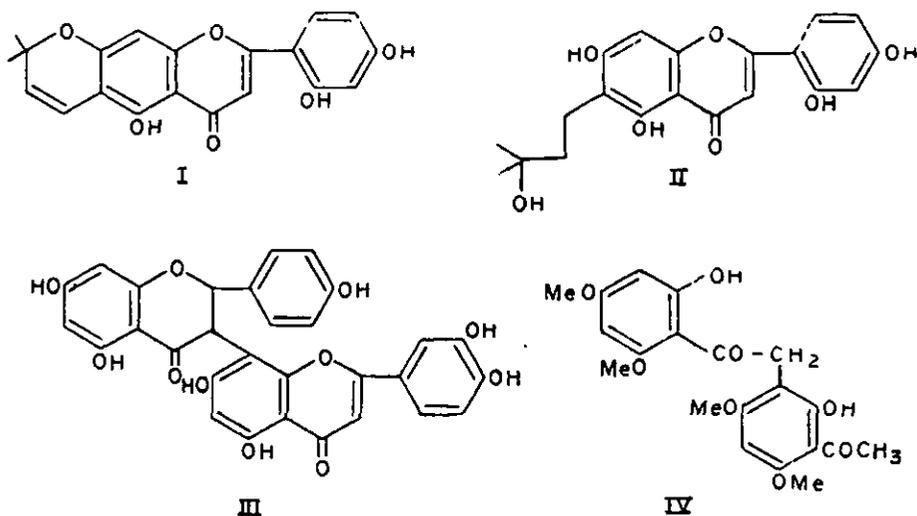
The phenolic constituents of wood play an important part in the technical utilization of wood. The object of the project is to isolate the phenolic constituents of certain woods, to determine their structures, study the relation between the phenolics in leaves, cambium, phloem, and xylem, investigate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

The work so far carried out relate to the following woods: *Salix tetrasperma*, *Artocarpus heterophyllus*, *A. hirsutus*, *A. gomezianus*, *A. lakoocha*, *A. incisa*, *Pinus longifolia*, *Morus alba*, *Garcinia morella* and *G. xanthochymus*.

The Indian variety, *Salix tetrasperma* contains friedelin and β -sitosterol besides a few phenolic glycosides, which have yet to be isolated and characterized. From the heartwood of *Artocarpus heterophyllus* two new flavones have been isolated and assigned structures (I) and (II). The heartwood of *A. hirsutus* contains all the pigments present in *A. heterophyllus*. *A. gomezianus* contains *meso*-erythritol besides a few known flavonoid pigments. *A. lakoocha* contains resveratrol, a trihydroxystilbene, besides β -sitosterol. The heartwood of *A. incisa* contains cycloartocarpin, artocarpin and norartocarpin. The barks of all the *Artocarpus* species have been examined and are devoid of any flavonoids. Dihydromorin, which has been reported to occur in *Artocarpus heterophyllus*, has not been encountered in any of the *Artocarpus* species examined by us.

From the barks of *Pinus longifolia*, we have isolated (+)-catechin and the presence of a number of flavonoids in trace quantities has been revealed. The barks of *Morus alba* contain a mixture of triterpenes from which betulinic acid has been isolated and characterized.

The structure of morelloflavone, a new biflavonoid from the heartwood of *Garcinia morella*, has been elucidated as (III) on the basis of the following data. By methylation with dimethylsulphate and potassium carbonate, morelloflavone gave a heptamethyl ether which on hydrolysis with 15 per cent ethanolic potassium hydroxide gave the deoxybenzoin (IV). Together with the UV, NMR and mass spectral data, these results led to the indicated structure for morelloflavone.



Work on the constitution of xanthochymol, a yellow colouring matter isolated from the fruits of *Garcinia xanthochymus*, is in progress.

Tissue culture : The tissues of *Artocarpus*, *Tectona*, *Morus*, *Pinus*, *Populus*, *Juniperus* and *Taxodium* were grown in different media. The callus growths vary to a large extent in the case of plant tissues of *Artocarpus*, *Tectona*, *Juniperus* and *Taxodium* in different media, and the others are selective. The possibilities of using these tissues for biosynthetic studies are being examined.

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PILOT PLANTS

1. *Aniline*

This important organic chemical is not manufactured in the country, and more than 1300 T/annum, valued at Rs. 25 lakhs are imported at present. Aniline salts (aniline hydrochloride, etc.) are also imported to the tune of 10-15 T/annum, valued at Rs. 2 lakhs. Aniline is listed in the manufacturing programme of HOC, Rasayani. Nitrobenzene, the chief raw material, is being produced in the country.

The process details for the vapour phase catalytic hydrogenation of nitrobenzene to aniline are being worked out using an indigenously developed catalyst.

After the successful working of a multi-tubular fixed bed reactor with 2 kg/hour capacity, a new pilot plant of 6 kg/hour has been installed. Units for the continuous distillation of the final product and recovery of aniline by extraction from the aqueous phase have been incorporated in the plant. The new plant was operated successfully with 97% conversion per pass. It is now proposed to run this integrated plant for several weeks, both for the purpose of evaluation and demonstration to project engineering firms who have shown interest in this process. Simultaneously the stability of the reactor is also under investigation.

2. *Carbonation of phenols*

Conditions for the production of BON acid by a wet process have been optimized on a scale of 3 kg/batch from statistical methods. Use of recovered β -naphthol for 10 successive batches (without affecting the yield and conversion) was found to be possible.

A realistic model for the Kolbe-Schmitt carbonation reaction has been formulated and the model tested by kinetic runs as well as by an independent series of mass transfer experiments. The process and the basic design data for 80 T/annum, plant are available. The work is now concluded.

3. Chlorination and hydrochlorination of ethylene

3.1 *Trichloro- and tetrachloroethylene*: These are versatile organic solvents used for various industrial purposes. Trichloroethylene is a widely used solvent in vapour phase degreasing of metal and metallic parts. The present largest use for tetrachloroethylene is in the dry cleaning of garments.

While the manufacturing licences have been issued for these chemicals in the private sector, they are not still made in the country and are imported to the tune of 2000 T/annum, valued at Rs. 25-30 lakhs. Their demand by 1970 is estimated as 15,000 T/annum, valued at Rs. 2.25 crores.

Attempts are being made to prepare these chemicals by chlorination of ethylene in a fluidized bed catalytic reactor. The reaction produces a number of chloroethylenes and chloroethanes. Conditions have been worked out to obtain trichloroethylene in 35% yield and tetrachloroethylene in 40% yield; however, consistency of the yields could not be achieved. The standardization of the reaction conditions are held up for want of a suitable analytical method to estimate different reaction products. Usual physical and spectroscopic methods are not found dependable. Chromatographic methods are in view. In view of commercial units which will soon go on stream, further work on this project is now stopped.

3.2 *Ethyl chloride*: Ethyl chloride is mainly used for the manufacture of tetraethyl lead which is added in petroleum fuels as antiknock agent and as an intermediate in other industries. At present more than 75 tonnes of ethyl chloride valued at Rs. 1.5 lakhs per annum are imported. The estimated demand of ethyl chloride in 1970 is around 3000 T/annum. The present indigenous production is based on ethanol as starting material. Equipment for the hydrochlorination of ethylene to ethyl chloride has been set up. Preliminary experiments indicated conversion of the order of 20% at atmospheric pressures. More detailed experiments are in view to optimize the process. An apparatus for carrying out the reaction at high pressure is also being fabricated. The above method of manufacture is of potential interest for areas where ethylene and hydrogen chloride would be available at site.

4. Design cell

The design cell is the outcome of several designs prepared by different groups. It has been created with the object of preparing chemical engineering designs (wherever necessary) for processes offered by the laboratory for commercial exploitation.

Chemical engineering designs for the following have been prepared :

1. Semi-commercial aniline plant, 60 T/annum.
2. Dibutyl and dioctyl phthalates plant, 10,000 T/annum.
3. Dimethyl and diethyl phthalates plant, 1,500 T/annum.
4. Dimethylaniline plant, 600 T/annum.

In addition, design drawings prepared by the project engineering firm for the opium alkaloids plant were checked and several modifications suggested. The engineering designs prepared by the HAL, Pimpri, for the production of vitamin C by the NCL process were scrutinized and improvements suggested.

5. *Dimethyl and diethyl phthalates.*

These are widely used plasticizers for cellulose plastics. At present they are not manufactured in the country on any substantial scale and major requirements are met through imports. It is further estimated that 1500 tonnes of these plasticizers valued at Rs. 90 lakhs will be required in 1970.

The main raw materials required for the manufacture of these important plasticizers are methanol, ethanol and phthalic anhydride. Methanol and ethanol are available in the country and phthalic anhydride will also be available in the near future, from Durgapur and Haldia projects.

Conditions for the preparations of above have been finalised on a pilot plant of 25 kg/batch. Both the phthalates can be produced in the same plant. In pilot plant trials yields upto 90-94% have been obtained.

Plant designs for the production of 1500 T/annum, of dimethyl and diethyl phthalates have been prepared. The process is ready for commercial exploitation.

6. *Dissolving pulp*

Investigations on different cellulosic raw materials available in India have been undertaken and their suitability for the production of dissolving pulp is being studied.

The indigenous production of dissolving pulps is at present of the order of 60,000 T/annum in the private sector while the licenced capacity is 1,85,000 T/annum. At the same time the imports of dissolving grade chemical wood pulps are more than 30,000 T/annum, valued at Rs. 4.5 crores.

In recent years eucalyptus hybrid species are being planted on large scale by a number of states in the country. According to the Advisory Panel for Dissolving Pulp Project (NCL), eucalyptus hybrid will be potentially important raw material in India for the production of pulp and paper in future.

Systematic investigations for the production of dissolving grade pulp by acid-prehydrolysis sulphate process have been undertaken and their suitability for the production of rayon and tire cord pulp is being assessed. Prehydrolysis conditions were studied by varying acid concentration, time and temperature of prehydrolysis, keeping pulping conditions constant. Under optimum conditions of prehydrolysis, pulp with following properties was obtained.

Ash - 0.14%; Silica - 71 p.p.m.;
 Fe - 79 p.p.m.; Pentosan - 1.8%;
 Cellulose - 96.8%; D.P. - 750;
 Filtrability - Fz - 39.

Comparative filtrability estimations of viscose solutions prepared from commercial soft wood sulphite, hard wood sulphate, and NCL two-stage alkali process pulp and acid prehydrolysis sulphate pulp from bamboo were worked out by varying carbon disulphide percentages in xanthation, and cellulose and alkali concentration in viscose preparation. Fz values for commercial pulps were found in the range of 35-56 while in case of NCL two-stage alkaline and acid-prehydrolysis pulps, the values were in the range of 84 and 79 respectively. According to the Advisory Panel for Dissolving Pulp Project (NCL), the two-stage alkaline pulp prepared in the NCL from bamboo has satisfactory chemical analysis except pentosan content.

Preliminary investigations of *Shorea robusta* by different processes have been worked out.

7. Fine Chemicals Project

This unit for the small scale production of different fine and speciality chemicals was started in April 1964. More than 300 chemicals are now being routinely prepared and offered for sale. A catalogue has been circulated to the various universities and research institutes. In response to repeated orders from different parties, phenoxy acetic acid (4 tonnes), chromatographic alumina (1 tonne), chromatographic silica gel (thin layer and column) (0.62 tonne) have been produced and sold during the year. Comparative figures for production and sales values of the unit for the year 1965-66 and 1966-67 are tabulated below:

<i>Year</i>	<i>Production</i> Rs.	<i>Sales</i> Rs.
1965-66	1,30,148	86,966
1966-67	2,82,821	1,86,597

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PRODUCT ORIENTED RESEARCH

PR.1 *Copper-promoted nickel catalyst for hydrogenation of vegetable oils*

Different varieties of catalysts are at present imported for the developing chemical industry in the country. The know-how for making these catalysts is a closely guarded secret and the indigenous technology in this field is not yet established. Attempts are, therefore, made to prepare some transition metal catalysts for oxidation and reduction reactions and to correlate their activity with their physico-chemical properties.

Nickel formate is a well-known material for the preparation of catalyst used for hydrogenation of fatty oils. A technique has been developed on laboratory scale (1 kg/batch) for the preparation of a nickel catalyst by the wet reduction of the mixed carbonates of nickel and small amounts of copper. Large scale trials revealed the difficulty in grinding the hard gel to the required fineness (below 350 mesh), which was overcome by modifying the co-precipitation technique so as to yield a soft opaque gel. This material could be easily reduced to the required fineness resulting in a product of very low bulk density and large surface area. The catalyst prepared from this gel was found to possess activity comparable to that of the commercially used nickel catalysts. The process is now available for commercial exploitation.

PR.2 *CdS photoconducting cell*

These cells find extensive use in visible and infra-red spectroscopy, exposure meters, temperature controllers and other control devices in industry. Photo cells are not at present manufactured on a commercial scale in India. The demand for such cells in the country is being assessed. It is believed that large quantities are imported at present.

Starting from cadmium sulphide a composition has been developed to obtain photosensitive crystal by sublimation process. A furnace for the crystal growth has been fabricated and operated successfully to prepare a number of crystals. The photo resistors so prepared show a change of four to five orders of magnitude in resistivity on illumination. They compare well with similar imported samples.

Various methods and techniques for the fabrication of devices using these cells have been tried out and the results are being evaluated. Circuitry for application of the photoconducting devices has been developed.

An illumination meter using the NCL photocell has been constructed and is in operation. A furnace temperature controller has been fitted with NCL photocell and is operating satisfactorily. Tests are being carried out on a number of photocells with a view to evaluate the following parameters useful for their application : (1) dark current (2) photocurrent gain (3) response time (4) ageing characteristics. A data sheet giving the characteristics of the three types of photo-cells developed in the NCL has been prepared and will be supplied to interested parties. The process for making these cells is now available for commercial exploitation. A vacuum deposition unit has been constructed using a newly developed vacuum gauge, and is operating satisfactorily.

A Hall effect measuring system using the latest techniques of Hall signal detection and provided with automatic recording facilities has been designed, fabricated, and is at present being used in the investigation of chemically deposited PbS films. The entire electronic system has been designed and built.

PR.3 *Piezoelectric ceramic materials having a general formula ABO_3*

These are widely employed as transducers for the generation of sonic and ultrasonic waves and in electroacoustic pickups etc. These products are not manufactured in the country on a commercial scale, and most of the requirements are at present met by imports.

During the basic studies on the dielectric and ferroelectric properties of various materials of the formula $Ba_x Pb_{\frac{1-x-y}{2}} Nb_y Zr_{1-y} O_3$, samples

having a ratio $\frac{x}{y} = 0.92$ showed high coupling coefficients, comparing well with some of the commercial P-Z-T materials. Selected samples are being evaluated.

PR.4 *Silicones and silicone intermediates*

The present widespread interest in organo-silicon chemistry stems very largely from the commercial importance of silicones $(R_2SiO)_x$. Industrial uses of silicones are now firmly established in Western countries as transmission fluids, antifoams, water repellents, high and low temperature lubricants, in mould release agents, in moulding compositions and chemically resistant elastomers.

In India, the applications cover many of the above mentioned fields, though the quantities involved are small so far. Accurate estimates of present demand/import are not available. Estimated requirement in the

electronic industry alone has been valued at Rs. 40 lakhs by 1974, calculated on the present price index. An Indian firm produced 32.12 tonnes of finished silicones in 1964-65 (year's consumption about 50 tonnes), valued at Rs. 11 lakhs.

Two CSIR laboratories are associated with this project arising out of a recommendation of the Get-Together of Research and Industry in December 1965. Preparation and study of the monomers and silicone intermediates will be carried out in the NCL, while development of formulations of oils, greases etc., suitable for specific purposes will be undertaken by the Indian Institute of Petroleum, Dehra Dun.

In the work taken up at the NCL in the last six months, acid-enriched ferrosilicon containing more than 90% silicon was used as the raw material for the direct synthesis of dimethyl dichlorosilane. A copper-impregnated material (300 g.) was reacted with methyl chloride in a suitably designed glass reactor which gave a mixture of the methyl chloro-silanes. There are several variables in the Rochow procedure (e.g. nature of coating on silicon, temperature range of reaction, composition and rate of flow of methyl chloride), and optimization is necessary by trial to get high yields of dimethyl dichlorosilane, the precursor of dimethyl silicone. A literature survey on the Rochow procedure has been made, and a market survey of silicones is under way.

PR.5 Ferrite compositions

Hard ferrites, which are permanent magnetic materials, are used in various devices such as cycle dynamos, loudspeaker magnets, latching magnets, and motors. These materials possess high coercive force and are very cheap when compared with other magnets. At present hard ferrites are not produced in India and the estimated requirement (in 1974) is of the order of 100 T/annum.

By proper choice of compositions, preparation procedure and addition of doping agents, it has been possible to prepare hard ferrites of high figure of merit. A barium ferrite composition (hard) containing suitable additives gave an energy product of $(1.3 \pm 0.2) \times 10^6$.

Soft ferrite materials which have high electrical resistivity are employed for high frequency use and are finding increasing applications in radio, television, radar etc. A soft Ni-Zn ferrite has been developed for medium wave application which gave $\mu Q = 38,000$ at 1 MC/sec. A Mg-Zn ferrite (soft) having a cut off frequency of 20 MC/sec. and μQ product of 5000 was also prepared. This composition avoids use of nickel and is substantially cheaper than other compositions known in the field.

All these compositions and their process know-how are available for commercial exploitation, and small samples will be supplied to interested parties.

PR.6 *Silicon tetrachloride*

Pure silicon tetrachloride is a raw material of primary importance in the preparation of semiconductor grade silicon and silicones. A unit for the production of 1 kg. of SiCl_4 per hour from ferrosilicon was fabricated and run successfully. Purification of the silicon tetrachloride so prepared was achieved to get a starting material suitable for the preparation of semiconductor grade silicon.

About 50 kg. of pure silicon tetrachloride produced in this unit was sold as a research chemical.

Preliminary experiments on the hydrogen reduction of pure SiCl_4 to give polycrystalline silicon have been successfully carried out.

PR.7 *Butyl titanate*

A technical preparation of butyl titanate is being standardized. At present the chemical is not manufactured in the country. The total requirement of the chemical in paint and other industries is being assessed.

PR.8 *Phosphors*

A low-cost process was developed for the preparation of zinc sulphide phosphor which finds use in fluorescent compositions and coatings. Calcium halophosphate phosphors used in coating fluorescent tubes were synthesized with various activators and co-activators. The potential demand for these materials is estimated around 50 T/annum.

Samples of mixed halophosphate phosphors of cadmium, magnesium and beryllium, using lead as sensitizer or primary activator and cadmium as secondary activator, were synthesized and their spectral energy distribution studied.

PR.9 *Chromatographic adsorbents*

The aim is to synthesize some inorganic chromatographic adsorbents from indigenous raw materials. Conditions were standardized for the preparation of calcium carbonate, calcium oxide, calcium hydrogen phosphate, calcium phosphate, magnesium oxide, magnesium carbonate, magnesium trisilicate and Fuller's earth for use in column chromatography.

A comparative study of chromatographic silica gel prepared in the Laboratory and two foreign samples of silica gel showed that our sample compared very well with the imported ones. Bulk quantities of the above mentioned chromatographic adsorbents were prepared and supplied to various outside parties through the Laboratory's Fine Chemicals Project. A TLC study was completed of some less frequently used chromatographic materials with respect to six Brockmann dyes.

PR.10 *Polytetrafluoroethylene*

Polytetrafluoroethylene, commercially known as Teflon (PTFE), is a corrosion- and heat-resistant polymer, finding ever expanding uses for gaskets, coatings, linings, frictionless bearings etc.

The tetrafluoroethylene monomer will be obtained by the pyrolysis of chlorodifluoromethane, for which a special graphite reactor for laboratory-scale experimentation has been fabricated.

PR.11 *Utilization of by-product fluorosilicic acid*

This by-product is available as an effluent (6-10% solution) in the superphosphate industry. On the anhydrous basis the availability is estimated around 2000-3000 T/annum.

Reaction between this effluent and mineral rock phosphate gave about 40% conversion to phosphoric acid at room temperature. Enhanced conversion upto 80% has been obtained at higher temperatures. The separation of phosphoric acid from CaSiF_6 by extraction with organic solvents is being investigated.

PR.12 *Diethyl-m-toluamide*

The compound is known to be a useful insect repellent and is widely used abroad. At present it is not produced in India.

Conditions for the preparation of diethyl-*m*-toluamide have been standardized on 0.1 kg/hour scale in a continuous reactor using *m*-toluic acid and diethylamine.

Since pure *m*-xylene is not indigenously produced, the mixed xylenes which are indigenously available have been oxidized to mixed toluic acids and the mixture condensed with diethylamine to give mixed amides containing approximately 60% *m*-isomer. This mixture as such has also been approved by A.F.M.C. Poona. Larger quantities of the product will be supplied for field trials.

PR.13 *Sorbic acid*

Sorbic acid is used as a preservative for food, bakery products and chapaties etc. A process for the manufacture of sorbic acid has been worked out on a laboratory scale and about 8 kg. supplied to Defence Food Research Laboratory, Mysore. The quality of this product is generally approved by them.

The conditions for the condensation of ketene and crotonaldehyde, which is the first step for the preparation of sorbic acid was successfully worked out in an improvised reactor at Kagaznagar under the guidance of NCL scientist. The party is now finalising arrangements to prepare this condensate on a large scale for its conversion to sorbic acid.

PR.14 *B. P.-grade lanolin*

Wool grease is a valuable by-product in wool combing. Indian wool does not contain recoverable quantities of wool grease, whereas imported marino wool contains as high as 19% wool grease.

There are two units in India producing raw wool grease from imported wool. One of the units produces approximately 150 tonnes of raw wool grease per annum.

The B.P.-grade lanolin (anhydrous pharmaceutical grade wool grease) is imported worth about Rs. 5-7 lakhs per annum. The imported B.P.-lanolin is largely consumed in pharmaceutical and cosmetic industries. The other grades of lanolin are used for rust prevention and are also employed in various industries such as paints, lubricants, printing inks, plastics and rubber.

At the suggestion of one of the Indian manufacturers of raw wool grease, conditions have been standardized to prepare B. P.-grade anhydrous lanolin and the samples are sent for evaluation. The economics of the process have been worked out on a unit of 1.5 tonnes of B. P.-lanolin per week and further negotiations with the firm are in progress.

PR.15 *para-menthane hydroperoxide*

This chemical is used as a catalyst for the low temperature copolymerization of styrene-butadiene in the manufacture of synthetic rubber. At present the entire needs of this catalyst, worth Rs. 5 lakhs/annum, are met by import.

The process for the technical preparation of *p*-menthane hydroperoxide from a by-product of an indigenous industry has been standardized on 5 kg. batch scale. The product and the economics of the process are being evaluated.

PR.16 *Synthetic glycosides*

Certain galactosides, thiogalactosides, fucosides and thiofucosides as well as other glycosides are used in studies in genetics and for other research purposes. The preparation of some of these products are not described in literature and involves specialized techniques. Some of these glycosides, worth \$800, have been prepared and exported to U.S.A. More than 12 glycosides have been prepared in the course of this work and a new method for the preparation of difficultly accessible aryl- α -glycosides has been developed.

PR.17 *Substitutes for gum Arabic*

Samples of some of the modified gums obtained from Ghatti, Karaya, Jeol gums have been supplied to the Post and Telegraph Board for large scale trials in different parts of the country. On the basis of actual trials, the P & T Board has approved some of the samples as substitutes for imported gum Arabic.

A systematic testing of the adhesive property of selected modified gum samples carried out in collaboration with ATIRA, Ahmedabad has revealed that they show two to three times more adhesive property as compared to that of gum Arabic. Commercial feasibility of production of the above modified gums is under examination.

PR.18 *Vitamin B₆*

The process for the preparation of vitamin B₆ has been earlier worked out on a laboratory scale as well as on bench scale. The process consists of ten main steps starting from chloroacetic acid.

The first three steps in the synthesis have been reinvestigated on laboratory scale and improvements resulting in the avoidance of the use of sodium have been effected. A completely new route is also being considered for investigation.

PR.19 *Cellulose caprate*

Cellulose caprate with requisite degree of substitution is the main ingredient of an optical cement composition. This is imported at present. The process for the preparation of cellulose caprate has been standardized on a laboratory scale.

PR.20 *Dithranol*

Dithranol is an anti-dermatitic agent and at present the entire demand is met by imports.

The bench scale process development work on dithranol has been completed in an overall yield of 53% by a two-step process starting with the potassium salt of 1,8- disulphonic acid of anthraquinone (available as 40% paste). The process is being offered to industry.

PR.21 Inulin from costus roots and its conversion to fructose

Fructose is a sugar tolerated by diabetic patients and is employed in the form of injections for cases of stress due to surgery and starvation. At present, fructose is not manufactured in India and the requirement is met by imports. Fructose is mainly obtained from inulin extracted from the plant *Jeruselem artichoke* which contains about 65% inulin. This plant is not grown in India; however, costus roots contain about 25% of inulin which may be a convenient indigenous source for fructose. Although the existence of inulin in costus roots was reported in 1929, no process for its economic extraction has so far been developed.

Conditions have been standardized for the extraction of inulin from costus roots (20 kg. batch scale) as well as from the powder remaining after the oil has been extracted. Inulin was obtained to the extent of 25% on the weight of the roots.

Hydrolysis of inulin to fructose was tried on a laboratory scale and fructose syrup in almost theoretical yields was obtained. Crystalline fructose has also been prepared from the hydrolysate.

PR.22 Analysis of organic compositions of industrial importance

A number of organic compositions available under trade names find special applications in different industries. Most of these are imported and their analysis to isolate and identify the components is undertaken with a view to see the feasibility of manufacture of similar compositions from indigenous raw materials.

Work has been undertaken to analyse four samples of surface active agents, as technical aid to a private industry. One sample was analysed and the composition reported. Three more samples will be analysed.

PR.23 o-Tolybiguanide (Sapanox)

The chemical is widely used as antioxidant for soaps and other cosmetics etc., under the commercial name Sapanox. Reported annual requirement which is at present met by imports of one of the leading soap and cosmetic manufacturers is around 3 tonnes valued at Rs. 90,000. Data from other commercial establishments in the field are being collected so as to assess the total requirement of the chemical in the country.

o-Toluidine and dicyandiamide are the two major raw materials required for the preparation of Sopianox. Although *o*-toluidine is not being manufactured in the country, it is on the manufacturing programme of an Indian dyestuff firm, while dicyandiamide is indigenously produced.

Conditions for the condensation of *o*-toluidine and dicyandiamide have been optimized on laboratory scale. It is proposed to prepare the chemical in the FCP unit and supply immediate requirements of the industry. The process is available for commercial exploitation.

PR.24 *Triethyl phosphate*

Triethyl phosphate is an essential catalyst in the manufacture of ketene from acetic acid. At present most of the need is met through imports by acetic anhydride manufacturers in the country. Ketene and diketene are becoming increasingly popular as versatile intermediates for a large number of useful products, and the demand for triethyl phosphate is on the increase. Triethyl phosphate is also used by the plastic industry as a plasticizer.

The object of the present investigation was to develop a process for its manufacture in the country with available raw materials. A commercially feasible technical synthesis of triethyl phosphate has been developed. Several bench scale batches (300 g.) were carried out in yields of over 95%.

A larger run is planned in a pilot plant unit being set up for the purpose. The process will be offered to industry on completion of pilot plant studies.

PR.25 *Dyes for synthetic fibres*

As mentioned in the earlier report, the object of this work is to synthesize newer and cheaper dyes for synthetic fibres which are gaining considerable popularity in the country. The present requirements are mostly met through imports. The work is also aimed at producing dyes with improved sublimation fastness properties. The synthesis involves the conversion of inexpensive acid dyes into water insoluble derivatives suitable for application to synthetic fibres like terylene, nylon etc. A series of reds, yellows, browns (Disazo), greenish blue (Anthraquinonoid) and greenish yellow dyes have been prepared and tested.

PR.26 *Reactive dyes*

The standardization of the technical preparation of a red reactive dye (Procion Red BS) was reported earlier. The parameters which affect the reaction were studied. Bluish red and violet dyes were also prepared by suita-

bly changing the diazo component and consistent results were achieved in runs carried out. An orange shade has also been produced.

PR.27 *Macrocyclic musk compounds*

Macrocyclic ketones and lactones such as exaltone, exaltolide, civetone, dihydrocivetone, ambrettolide, isoambrettolide are valuable perfumery materials. New efficient methods of syntheses of these compounds from cheap raw materials have been developed and standardized.

These are not manufactured in the country; however, it is believed that similar ones are imported under different trade names. The total requirement of these compounds in different industries and the potential demand for them in foreign countries are being assessed.

Starting from vegetable fatty acids (C_{14} to C_{17}) the corresponding acyloins are obtained through their diesters. The resulting cyclic hydroxy ketones are reduced to their respective macrocyclic ketones. Based on the fatty acids the overall yields of these perfumery ketones are in the range of 15 to 20%. For the syntheses of macrocyclic lactones, hydroxy fatty acids of the same range are polymerized to yield polyesters, which are further depolymerized to obtain the monomer lactones. The overall yields are in the range of 20-25%.

During this year, about 100 g. of exaltolide and 1.4 kg. of exaltone were prepared for sale (valued at Rs. 600 and Rs. 7,000 respectively).

The acyloin condensation step and the final reduction of acyloin have been improved and a batch size of 1 mole of diester (300-400g.) with lesser amount of xylene (used as entrainer) has now been carried out successfully.

All these processes are available for their commercial exploitation.

PR.28 *Transformation products of citral*

India produces lemongrass oil in large quantities mostly in Kerala state. Lemongrass oil worth Rs. 1.3 crores/annum is being exported at present. It has been observed that although the consumption of various perfumery and pharmaceutical products made from citral (the main constituent of lemongrass oil) is increasing, the export of Indian lemongrass oil has been steadily decreasing. The decrease in export is mainly due to the synthetic manufacture of citral in some of the foreign countries. At the same time the internal demand for citral has also considerably increased. The situation warrants more outlets for the economic utilization of citral available from indigenous natural source.

Attempts are being made to transform citral to marketable perfumery materials such as linalool, *dl*-citronellal, citronellol, geraniol etc. Citronello

is being produced in the country from the imported Java citronella oil, and the production is reported to be 20T/annum, valued at Rs. 25 lakhs. *dl*-Citronellal is a starting material for the manufacture of *dl*-menthol which may find increasing market in the pharmaceutical industry. Linalool and geraniol also are established perfumery materials.

Besides modifying known methods of such transformation, altogether new methods are being studied. Citral epoxide is the key intermediate for the synthesis of linalool. Citral has been successfully converted to epoxide in high yields (paper 97). Attempts to improvise yields of linalool from citral epoxide are in progress.

A new one-step method has been successfully developed for the conversion of citral to high purity citronellol in good yields. The process is being evaluated for its commercial exploitation. If found economically feasible, the process may result in substituting imported Java citronella oil.

PR.29 l-Menthol and dl-menthol from d and dl-citronellal and preparation of dl-citronellal from citral

This work has been undertaken to develop a synthetic route for *l*-menthol and *dl*-menthol from indigenous raw materials. *dl*-Menthol (B.P.) was prepared from *dl*-citronellal, which was obtained by the reduction of citral, through the usual reactions of cyclisation, catalytic reduction, oxidation, and reduction etc. The samples of *dl*-menthol have been sent to various firms.

VPC analysis of *dl*-menthol shows the presence of 80% menthol and 20% isomenthol.

PR.30 Development of stationary liquid phases for GLC instruments

In all types of GLC instruments, which are at present largely used in research and industry, different liquid phases and supporting materials are employed. These are at present totally imported. With the growing tendency of using GLC techniques in different fields, the demand for these phases and supporting materials will be considerably increased.

Attempts have been made to use Indian firebrick powder as a supporting material. Various physical properties such as packing density, surface area, porosity and surface activity were studied in detail. Necessary pre-treatments have been developed to standardize the base material. Preliminary evidence has shown that the columns with this newly developed base are as efficient as those prepared from imported supporting material.

Different high boiling polyesters are being studied as liquid phase absorbents, to be used along with the above base. In a novel method for an

efficient impregnation of the liquid phase on the base, the hydroxy monomer was successfully polymerized on the supporting base and the required polyester was formed *in situ*. Several other polyesters are being tried for their suitability as liquid phase absorbents.

PR.31 *Ion exchange resins*

Ion exchange resins are widely used mainly for industrial demineralization of liquids. Operational simplicity and regeneration of resins are the chief advantages in the use of ion exchange resins. Cation and anion exchange resins having low as well as high capacities have been prepared in both granular and bead forms and their applications and performances in different fields studied.

31.1 *Styrene-DVB cation-exchange resin* : Physical properties and attrition resistance of the finished resin have been substantially improved by certain modifications in the preparation of the copolymer, sulphonation of the copolymer beads and their subsequent hydration. Complete details of these modifications have been communicated to the three licencees to whom the original process had been released.

The sulphonation step has been further modified (10 kg/batch scale) by employing a catalyst which reduced the amount of acid required, thereby lowering the final price of the resin.

31.2 *Styrene-DVB anion-exchange resin* : The process reported earlier has been modified, thereby reducing the cost of production of the resin, by avoiding the use of swelling agent while aminating the chloromethylated copolymer with trimethylamine. The results have been confirmed on 10 kg/batch scale.

In order to increase the capacity of another type of anion exchange resin using dimethylamino-ethanol for amination, work has been undertaken to improve upon the degree of chloromethylation of the copolymer.

Since the chloromethyl ether required in the above process was not available in the country, conditions were standardized for its synthesis and large quantities were prepared.

31.3 *Acrylic-base cation-exchange resin* : These resins are mainly used in pharmaceutical and antibiotic industries. At present they are not manufactured in the country and the requirements are wholly imported. The annual make-up requirement of the four antibiotic units in the country is estimated at about 9,500 kg/annum. Since the make-up requirement of these

resins is only 2-5 % of the original feed, it appears that large quantities of this type of resins will be required for any new pharmaceutical and antibiotic units which will employ ion exchange treatment in the future.

Experiments for the preparation of this type of resin, which is a copolymer of methacrylic acid and divinyl benzene, have been undertaken. For immediate work methacrylic acid was prepared from methyl methacrylate. Resins prepared with varying percentages of divinyl benzene are being tested for their physical properties and column operations.

PR.32 *Application of ion exchange resins for the preparation of pectin from citrus peels*

CFTRI, Mysore have developed a process for the recovery of pectin from citrus peels by using acid extraction and precipitation of pectin by alcohol. This process was simplified and improved by making use of ion exchange resins developed in the NCL. With the use of the suggested method, it is now possible to obtain pure pectin in one step. The process was demonstrated to CFTRI scientists for application of this technique on a large scale.

PR.33 *Polystyrene foams*

Polystyrene foams are mainly used in India for low temperature insulation. They are also employed as packaging materials especially for packaging of delicate instruments etc. At present one firm in the country is manufacturing this product to the tune of 600 T/annum, using imported know-how. Although there are no imports of similar products, the demand in the country is expected to be much more than the indigenous production.

Preparation of free-flowing expandable polystyrene beads has been standardized on 2 kg/batch scale. Semi-automatic pre-expander was designed and operated successfully. A large size tray-type pre-expander and a mould for preparing large size foam sheets have been fabricated for trials. Many industrial firms have already shown interest in this process.

PR.34 *Formaldehyde polymers*

A useful class of plastics with improved chemical and mechanical properties substituting non-ferrous metals used for handles, knobs etc., has been developed in USA and Germany and their demand is rapidly growing.

These plastics are polymers based on formaldehyde. Since formaldehyde is now available in India, exploratory work to prepare the intermediate trioxane from *p*-formaldehyde has been undertaken.

PR.35 *Surface coatings*

35.1 *Styrenated alkyds* : Coatings based on styrenated alkyds are known to possess superior properties than the normal alkyds. A satisfactory composition of the styrenated alkyd based on high and medium oil length has been developed to meet the requirement of a good surface coating in all respects. Number of samples were sent to different parties for evaluation and favourable performance reports have been received. Scaling up the batch size of the process has been undertaken and the process will be shortly available for commercial exploitation.

35.2 *Linseed oil emulsions* : These new products have been developed in USA. Linseed oil base emulsions compare well in performance with the now available plastic paints based on acrylic and polyvinyl acetate emulsions. It is hoped that paints based on linseed oil emulsions will replace the above plastic emulsion paints due to their low cost.

It has been found that refined linseed oil of pale yellow colour (not double boiled linseed oil) is useful for this purpose. Conditions of polymerization of the oil have been studied so as to produce a highly viscous pale yellow product. Emulsions prepared from this product can be thinned down to any dilution. Properties of the coating, based on these emulsions will be evaluated, followed by large scale preparation of the finished product.

PR.36 *Upgrading of rosin*

At the initiation of a rosin manufacturing firm, this *ad hoc* work has been undertaken to improve the colour of the samples sent by the firm. A few samples were treated and the colour could be improved to some extent. Upgraded samples are being sent to the party.

PR.37 *Sponge textile*

Latex foam backed textiles find use as floor covering, carpets, and upholstery. These are not yet produced in the country on commercial scale. It is expected that, when introduced, they will find substantial market. Preliminary experiments have shown encouraging results, and the follow-up of the project on large scale will be undertaken if sponsored by some interested party.

PR.38 *Polycaprolactam powder for chromatography*

Conditions have been standardized to prepare a fine polycaprolactam powder from polycaprolactam waste. It is found to be a suitable

chromatographic adsorbent, particularly for some natural dyes. About 30 kg. were produced and used in the laboratory. Regular production of this item will be undertaken in the FCP unit.

PR.39 *Adhesives*

39.1 *Cement for diamond setting*: Special cement, used for setting the diamonds for polishing, is at present imported. The Indian diamond industry has been hit by the non-availability of this cement. Attempts have been therefore made to prepare a comparable product. Two samples of the cement based on synthetic resins have been prepared, and sent to an interested party for evaluation.

39.2 *Adhesive for staple pins* : An adhesive composition for use in bonding staple pins was developed and tested on automatic machines used in the fabrication of staple pins. Accordingly, some modifications are being introduced in the composition and a bulk quantity of the modified product will be sent for further trials.

39.3 *Self-sticking composition for paper labels* : At the initiation of Ministry of Home Affairs, a special composition of the above type was developed and samples were sent for evaluation. The preliminary reports are satisfactory and further work will be undertaken shortly.

PR.40 *Polyurethanes*

Polyurethanes is a class of polymers which are formed by condensing polyhydric alcohols with polyisocyanates. During the last ten years, polyurethanes of varying chemical and physical properties have been developed in some of the advanced countries and are being employed for a wide range of industrial applications such as rubbers, fibres, foams, coatings and adhesives.

In India, the polyurethane technology is still in an infant stage. Besides polyurethane foams, being prepared with imported technology and raw materials, neither the polymers nor their end products are commercially manufactured in the country. Although polyisocyanates are not yet manufactured, it is hoped that they will be available in commercial quantities in the near future. The other counterpart of these polymers e.g. polyhydric alcohols derived from sebacic and adipic acids, can be made in the country.

The know-how for the preparation of these polyhydric alcohols has already been developed, and work on the preparation of a series of modified polyhydric alcohols of desired properties based on castor oil has been carried out. Based on CNSL, the know-how for the preparation of a few polyisocyanates has also been obtained.

During the period under report, the following polyurethane compositions have been developed:—

40.1 *Coating for nylon fabric* : At the initiation of SASMIRA, Bombay, compositions based on polyadipate and polyisocyanate were successfully prepared for coating nylon fabric. Nylons coated with this type of compositions are used for making high altitude hutments etc. The final report on the performance of coated nylons (with a selected coating composition) is awaited.

40.2 *Adhesives* : The isocyanate type adhesives are known to have superior bond strength for metal-metal, metal-rubber, rubber-fibre, rubber-leather and rubber-rubber joints. Adhesive formulations prepared from CNSL and phosgene have been prepared and tested for rubber-leather, rubber-rubber and rubber-fibre adhesions. These compositions are being further evaluated for their possible commercial uses.

Coating of CNSL-based isocyanate compositions are further found to give good water repellent properties to synthetic and natural fabrics employed for making raincoats, umbrellas, and shower-proof clothes. Large scale preparation of these compositions have been carried out and these are being systematically evaluated at SASMIRA, Bombay and ATIRA, Ahmedabad. Parties interested in these products are being approached for large scale performance trials.

40.3 *Typewriter rollers* : The typewriter rollers available in the market are usually made of imported synthetic rubbers. A new castor oil-based composition has been developed and a few rollers of desired shore hardness were moulded. These were tried by some leading typewriter manufacturing firms, and were found to show good performance for typing nine copies at a time. The moulding technique is further being modified so as to obtain a uniform product. The economics of the preparation of typewriter rollers are being studied.

40.4 *Urethane rubbers* : Using modified castor oil or polyesters as polyhydric base, number of urethane rubbers have been prepared and their chemical and physical properties studied in detail.

One of the rubber composition evolved out of these basic studies has been successfully employed for the manufacture of typewriter rollers mentioned above. Another one has been tried for making oilseals for automobiles. The performance of this rubber is being evaluated.

40.5 *Printing rollers* : It was pointed out, by some of the parties who purchased the know-how of this process, that some of the rollers produced were brittle in character. Hence the problem was looked into. A fresh and entirely new process with improved physical properties of the printing rollers was developed and the know-how given free to all the parties who had acquired the licence from NRDC for manufacturing these rollers.

40.6 *Composite propellents*

A castor oil based formulation for making composite propellents has been developed. These compositions have been sent to Thumba Research Station, Trivandrum for evaluation.

PR.41 *Utilization of coir pith for gaskets*

At the initiation of a coir factory, coir pith was processed to prepare rubber gaskets of varying types employed in different fields. Samples prepared have been sent to different parties for evaluation. This work may find a ready use for this waste material available with Indian coir factories; it may also partly substitute imported cork.

PR.42 *Studies in CNSL*

Exploratory work on cashewnut shell oil for the preparation of different industrially useful chemicals in plastics and rubber field is being carried out.

Antiozonants and antioxidants for rubber, based on tetrahydroanacardol and possessing urea linkages, have been prepared and tested.

Attempts are also being made to prepare epoxy-base compositions from CNSL. These are being evaluated as stabilizers for PVC.

PR.43 *Oil filter papers*

At the initiation of a private party engaged in filter paper manufacture, a coating composition has been developed for making oil and air filters. Samples prepared in the laboratory were tested by an oil engine manufacturing firm and were found satisfactory. The coating technique is being standardized for large scale trials.

These special filter papers are at present imported in large quantities and are not produced in the country. Demand for such papers in different fields is being assessed.

PR.44 *Rubber-base adhesives*

Many rubber-base adhesive formulations are used for binding metal-metal or metal-rubber joints. One such adhesive required by HAL, Bangalore has been successfully prepared which satisfied most of the specified requirements. The adhesive was prepared in large quantities and has been sent for further trials.

Another rubber-base adhesive formulation was developed for sealing water tanks made of synthetic fibre. The performance trials of the adhesive, conducted by the interested party, have been successful. The composition is being evaluated for commercial exploitation.

PR.45 *Rubber reclaiming agent*

At present about 10,000 T/annum of reclaimed rubber is manufactured in the country. It is estimated that this may increase to a target of 25,000 T/annum in 1970-71. Based on the use of 1% of reclaiming agent in the reclaimed rubber, the present consumption of imported reclaiming agent is around 100 T/annum, valued at Rs. 10 lakhs. The corresponding figures for 1970-71 requirements will be 250 T/annum, worth Rs. 25 lakhs.

With a view to develop indigenous know-how in this field, technical preparation of a reclaiming agent of the 'Renacit' type has been standardized on 2-5 kg/batch scale. The product was tried in one of the reclaiming plants in the country and was found acceptable. The process is now being evaluated for commercial exploitation.

PR.46 *Rubberised cork sheets*

Systematic study on the incorporation of cork granules into natural and synthetic rubbers so as to obtain sheets with good tensile strength, compression set, aggregate resistance, resistance to shrinkage and with standard hardness number was carried out.

Rubberised cork sheets prepared by this process proved equivalent to the imported ones and a satisfactory process demonstration of the same was given to the firm licensed to utilize the process.

PR.47 *Polymerization of turpentine fractions*

Indian turpentine oil contains a large proportion of Δ^3 carene and with a view to find useful applications of carene, some studies on its polymerization have been initiated.

Polymerization of Δ^3 -carene using BF_3 , AlCl_3 , SnCl_4 and TiCl_4 as catalysts gave a very small proportion of a polymeric material. The major portion of the resultant product was found to be a dimer. The dimeric products were not found much useful as plasticizer for PVC and although they were compatible with natural rubber, no useful properties could be imparted to rubber mix. No useful products were obtained in the attempts of making copolymers of Δ^3 -carene with styrene and α -pinene. Work on this problem has been discontinued.

PR.48 Recovery of light and heavy pyridine bases from their aqueous solutions

Mixtures of pyridine, picolines and higher homologues are commercially known as pyridine bases. They are often used as solvent or medium wherein the bases are not actually consumed, but merely contaminated by impurities or diluted by water. In such instances, they are recovered for re-use.

Salting out with alkali, a commonly practised procedure for this recovery, consumes large quantities of alkali which is wasted in the process. The operating data for other methods based on distillation are not readily available.

The present work was undertaken for a private firm to develop a more economic method for pyridine recovery from aqueous lyes. Binary azeotropic distillation followed by the benzene azeotropic distillation of the concentrated distillate was tried on the samples supplied by the firm. This gave a colourless product with minimum operations. The recovery of pyridine bases was approximately 95% and loss of benzene used as an entrainer, about 3%. The method was recommended to the party with the necessary process data. Subsequently, other methods such as (i) combination of biphasic separation, solvent extraction and subsequent benzene azeotropic distillation, (ii) direct hot solvent extraction followed by benzene azeotropic distillation, were also tried and found to give good results.

PR.49 Preparation of methylol stearamide

Methylol stearamide is an important constituent of water repellent compounds used in textile industry.

The Bombay Textile Research Association, Bombay (BTRA) which developed a process for this chemical on a laboratory scale requested NCL's help to prepare it in sufficient quantity for mill trials. Pilot plant facilities were provided for the purpose. Based on BTRA's work the following steps were carried out. (i) Purification of stearamide (ii) preparation of methylol stearamide by reacting stearamide with formalin, and (iii) purification of methylol stearamide.

Work carried out on 5 kg. batches of the final product, with close collaboration of BTRA's scientists, gave the final product of the desired specifications.

PR.50 *Vitamin C and sorbitol*

Based on pilot plant trials conducted at NCL, a project report for a plant of 50 T/annum was prepared and submitted to M/s Hindustan Antibiotics Ltd., Pimpri, to whom a licence for the manufacture of vitamin C (125 T/annum) has been given. The plant designs submitted by the HAL staff have been scrutinized.

The process for the production of sorbitol from glucose was worked out on 10 kg/batch scale and conditions have been standardized. This process has also been given to M/s HAL for their vitamin C plant.

To cut down the cost of production of sorbitol, the hydrogenation of invert sugar to give sorbitol and mannitol is being worked out. The conditions for the inversion and hydrogenation of invert sugar and the separation of sorbitol and mannitol obtained have been standardized. Various chromatographic methods to determine the purity of the resultant products are being tried.

PR.51 *Technical preparation of 2,4-dinitromonomethyl aniline*

This is an intermediate for the preparation of tetryl. It is at present manufactured by the oxidation of dimethylaniline. Since this preparation is hazardous, it has been proposed to prepare it by nitration of 2,4-dinitromonomethyl aniline.

Conditions for the preparation of 2,4-dinitromonomethyl aniline from the 2,4-dinitrochlorobenzene and methylamine have been standardized and the product was tested and found to be satisfactory. 50 kg. batch was successfully tried.

PR.52 *Phenacetin*

Phenacetin is a widely used chemical in the pharmaceutical industry. About 179 tonnes valued at Rs. 11 lakhs were imported during 1965-66.

Acetylation of *p*-phenetidine was carried out in the presence of an entrainer, and it was observed that the reaction could be completed with 97% yield within about six hours. Pilot plant runs on 40 kg/ batch of phenacetin are being carried out to collect the necessary engineering and process data.

PR.53 *Monoethylaniline*

Monoethylaniline is an important intermediate required in the manufacture of certain explosives. The total demand is estimated to be around 100 T/annum, valued at Rs. 10 lakhs.

A bench scale unit for the continuous ethylation of aniline was successfully worked. Based on these results, conditions were standardized on a small pilot plant of 3-4 kg/hour capacity.

Process design for a plant of 100 T/annum is under preparation, and the working of the plant is proposed to be demonstrated to interested parties.

PR.54 *Aliphatic amines*

54.1 *Methylamines* : Methylamines are used in the manufacture of herbicides and fungicides, textile chemicals, rubber accelerators, photographic chemicals and in medicine. They are not at present manufactured in the country and are imported either as such or in the form of their derivatives. Imports of these amines are not separately classified. However, it is gathered that monomethylamine derivatives, mostly medicinals, worth Rs. 5 to 7 lakhs are imported in the country. By the end of the fourth five-year plan period, demand to the extent of about 38 T/annum of monomethylamine has been estimated for medicinals alone.

Demand for all the three methylamines in the country is estimated around 3-4 thousand T/annum, valued at Rs. 2 crores. Details of individual demands in different fields are being collected. These amines can be produced in the same plant by reacting methanol with ammonia in the presence of a catalyst. The ratio of the three methylamines produced in this reaction is controlled by the ratio of reactants and by the reaction temperature. Both the raw materials are now available in the country.

A bench scale reactor has been set up with suitable accessories. Ammonia and methanol are reacted over a catalyst to form a mixture of methylamines. Another assembly made of glass has been set up for a kinetic study of the reaction. Conditions are being worked out for the identification and separation of the different amines formed in the reaction.

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

At present the chemical is not produced in the country and more than 34 tonnes worth Rs. 2.5 lakhs were imported in 1965-66. The demand for pesticide manufacture alone is estimated around 550 T/annum, and the total projected demand for 1970-71 would be around 1200 tonnes, valued at Rs. 90 lakhs.

Ammonia and ethylene dichloride are the main raw materials for the manufacture of ethylenediamine. Both the raw materials are now available in the country.

In a batch reactor (25 litre capacity) ethylene dichloride and liquor ammonia are reacted to form ethylenediamine as the principal product. Small quantities of other polyamides are also formed. Statistical optimization of the process conditions is in progress.

PR.55 *Dimethylaniline*

This is an important intermediate for dyestuffs and for the manufacture of certain explosives. It is not produced in the country, and during 1965-66, 380 tonnes of dimethylaniline worth Rs. 7.6 lakhs (c.i.f.) were imported. The demand is estimated around 600 T/annum, valued at Rs. 30 lakhs at the current price.

Pilot plant trials for the reaction of methanol and aniline (9 kg/batch) were successfully completed with an overall yield of 95% for a 99.5% pure product. The process is now available for commercial exploitation. Work on the development of a continuous process is being continued.

PR.56 *Foundry chemicals*

The Indian foundry industry has made good progress in recent years. At present, there are over 5000 small and big foundries in the country which produced variety of castings required in engineering industry. In the context of the rapid expansion of foundry industry and the increasing demand for castings of close tolerance limits, the development of an indigenous foundry chemical industry is important. Processes for the production of some of these chemicals are being developed employing indigenous raw materials.

56.1 *Shell moulding resins* : Shell moulding technique is generally followed to produce good quality precision castings, and the resins used are of phenol-based thermosetting ones. Efforts have been made to substitute phenol, which is at present imported, and evolve suitable compositions based on CNSL-formaldehyde and urea-formaldehyde type resins. Sand core specimens using these resins were made and tested for their green strength finish, setting time, curing, non-sticking and baking characteristics.

56.2 *'Sinol' type core binder* : The binder is specially suitable for steel castings giving good dry and hot strength.

A composition based on sulphite liquor has been developed. Field trials were carried out in some of the leading foundries and the product was found comparable with the imported one. The process is being scaled up. The market potential of the product is being investigated.

56.3 *Dry core binder* : This binder contains starch and is usually used in small foundries. Although it is simpler and easier to work with, it gives off smoke during pouring operation and thus leads to production of defective castings with blow holes. Efforts have therefore been made to prepare a cheap dry core binder without starch and without undesirable smoking characteristics.

A composition based on lignosulphonic acid condensate has been worked out on 1 kg. scale. Sand core specimens were made using this binder and tested for green strength, physical and baking characteristics. Encouraging results have been obtained. Arrangements are being made to produce it in larger batches and the product will be further evaluated in large scale field trials in foundries.

56.4 *Double boiled linseed oil substitute* : Double boiled linseed oil is conventionally used as a sand binder in foundries. The oil also finds applications in many other fields. Efforts were made towards the substitution of this oil by developing a cheaper composition from indigenous raw materials. The composition was prepared on 100 kg/batch scale and was found useful in field trials. The process is ready for commercial exploitation.

56.5 *Barrier cream* : The handling of various types of binders and chemicals by foundry workers can cause dermatitis. Use of barrier cream offers protection against this.

A cheap composition has been worked out from indigenous raw materials on 1 kg/batch scale. Larger batches of the product will be made for consumer acceptability trials.

PR.57 *Starch phosphate* :

Starch phosphate finds manifold applications as thickeners in canned foods, salad dressings, in wheat flour dough for bread, as binders in pharmaceuticals and as a flocculant, etc.

Starting from indigenously available tapioca starch, compositions with varying phosphorus content were prepared. The products are being tested for their characteristics.

PR.58 *Vapour phase chromatograph*

The vapour phase chromatograph is finding increasing application as a versatile and powerful analytical tool in both the chemical research and industry. The demand for these instruments is increasing rapidly and a market survey has shown it to be several hundred units in the immediate future. These instruments are presently imported mainly from USA and UK, and the cost varies from Rs. 25,000 to Rs. 50,000 for each unit.

A vapour phase chromatograph, incorporating most sophistications which are available in the better class of modern instruments, has been developed. Work on this project has resulted in a gas chromatograph with a dual column system, electronic temperature control and programming in the range 30-300°C, a thermal conductivity as well as a flame ionization detector system. Except the recorder, the instrument utilizes indigenous materials only. Full specifications are available on enquiry. The know-how is being released to industry for commercial production of the instrument.

PR.59 *Electron spin resonance spectrometer*

An ESR spectrometer working in the x-band (3 cm. wavelength) microwave region is under development. The various units required for this equipment, viz. (i) magnet system with regulated power supply (ii) sweep and modulation generators (iii) microwave generating system using a reflex klystron and the associated regulated power supplies (iv) the microwave transmission and resonant cavity system (v) crystal detector, preamplifier and lock-in-amplifier system, and (vi) display and recorded system, have been designed and built as prototypes. The various units have been assembled and tried out as an ESR spectrometer with a number of standard and other samples. Its sensitivity has been found to be of the order of 10^{13} spins/ ΔH and the resolution to be quite satisfactory.

Work on designing of a suitable console and the layout of the various controls for convenient operation is being taken up, on completion of which a suitable prototype of the spectrometer will be built and tested.

The ESR spectrometer is finding an increasing application in the study of free radicals in solution, crystals and living tissues, lattice defects in crystals, metals and semiconductors, radiation damage and numerous other fields. The instrument of the type under development, which is expected to be relatively inexpensive, will be useful in research and teaching.

PR.60 *Construction of a precision ultrasonic interferometer*

The instrument is useful in studying thermodynamic data of solutions such as adiabatic compressibility, specific heat at constant value and apparent molal properties.

A complete unit according to our design has been fabricated and tested. The instrument mainly consists of a 5-MC crystal oscillator with a stabilized frequency and power supply, a ratio bridge consisting of a three matched 52-ohm resistor and the ultrasonic cell as the fourth arm a DC-difference amplifier to compare the off balance signal of the ratio bridge with the bridge input voltage, and a detector. The ultrasonic velocity in water has been determined with this instrument at 25° as (1496.05 ± 0.8) m/sec. which is comparable with recently published values.

PR.61 *Preparation of biochemicals*

Preparations of the following costly biochemicals have been standardized and samples have been sent to the biochemical units of the CSIR and the University of Delhi for distribution and evaluation. These biochemicals are required by various Indian and foreign research institutes.

1. D₆(+)-isocitriclactone
2. (—)-citramalic acid (Na-salt)
3. (+)-citramalic acid (Na-salt)
4. dl-citramalic acid (Na-salt)

Experimental conditions for the preparation of methyl and benzyl viologens on a laboratory scale have also been standardized for the FCP.

□ □ □

RESEARCH PROJECTS

RP.1 THEORETICAL INVESTIGATIONS ON SOLID STATE AND MOLECULAR PHYSICS

It is now well established that solid substances having interesting semi-conducting, superconducting and magnetic properties are finding newer practical applications in the fabrication of solid state devices employed in various electronic industries.

An understanding of the basic properties involving the interactions of electrons, phonons and spins in various solids is a necessary prerequisite to the practical development of new devices. With this aim in view, following theoretical investigations have been undertaken.

1.1 *Interactions involving conduction electrons in magnetic metals and alloys*

Earlier the interaction between conduction electrons and impurity states were studied taking into account s-d mixing and exchange interactions.

The possible mechanism of resistance minimum in dilute alloys with transition element impurities which do not show localized magnetic moment has been formulated. The interaction consists of a combination of potential scattering of conduction electrons by impurity coupled with exchange interaction of the conduction electron with the electrons of the impurity atoms. In the formulation, the role of both empty and occupied impurity states is taken into account. The resulting expression has the form :

$$\rho(\text{Total}) = aT^5 + c\rho_r - c\rho_s^0 T$$

where c = concentration of impurity and a , ρ_r , $\rho_s^{(0)}$ are appropriate coefficients and T is the temperature. Actual comparison shows that in titanium containing transition element impurity a resistance minimum does occur at around 20° K. This is in agreement with the available experimental results.

This study has been extended to dilute alloys having localized magnetic moments (Mn in Ag; Fe in Au, or Cu etc.) and the occurrence of resistance minimum and giant thermoelectric power in them has been explained.

1.2 *Superconductivity in metals and alloys*

Various physical factors which influence the transition temperature of superconductors are being studied since superconductors with high transition temperatures will open up numerous avenues for practical applications. The effects of pressure and impurities were studied and a theoretical mechanism was developed to explain the increase or decrease of superconducting transition temperatures.

The occurrence of high transition temperatures in certain superconducting systems such as V_3Si , Nb_3Sn etc., has been examined in relation to their structures and other physical factors. For this purpose the effect of one-body spin independent interactions involving conduction and localized electron states taken in conjunction with phonon induced attractive electron-electron interaction was analysed. The method of double time Green's function was followed in the formulation. Thus the one-body interaction terms which arise from structure effects seem to be responsible for enhancement of transition temperature in superconductors. It has also been shown that in very thin films of superconductors an additional mechanism comes into play owing to transverse quantization of electronic states, thereby increasing the transition temperature. These effects are very promising for the development of high transition temperature superconductors.

1.3 *Phonon-magnon interactions in magnetically ordered solids*

The object is to find out the basic mechanism of interactions involving phonon and magnon excitations in magnetic solids. Atomistic theories of interaction processes involving acoustical phonons and magnons in ferro-, antiferro- and ferri-magnetic systems have been completed and the rate processes determined. Study of thermal conductivity and magnetizations of manganese ferrite and magnetic garnets was also completed.

Taking into account the above interactions the renormalization of the energy spectrum of the phonon and magnon modes was carried out. The renormalized phonon modes show that there will be change in the Debye temperature at the Curie point of the magnetic systems. The renormalized spin wave frequency shows that instability in the acoustic mode may develop in the high temperature region. In order to formulate the co-existence of magnetic and ferroelectric phases the interactions between polarization waves and spin waves were studied in magnetodielectrics. For this purpose the role of optical phonons and magnons was taken into account. Relaxation frequencies for such processes in antiferro- and ferri-magnetic systems were calculated at various temperatures. It was found that the contribution of optical phonon-magnon interaction becomes quite appreciable at $25^\circ K$.

This work was extended to the study of interactions between neutrons and magnons in ferro- and ferri-magnetic systems. The neutron scattering cross-section depends on temperature in different powers.

1.4 *Exchange interaction in magnetic solids*

In the last few years indirect exchange processes in magnetic compounds were studied.

Taking cognisance of mixing and exchange interactions between impurities and its neighbours in dilute alloys (Fe in Pd) the origin of giant magnetic moment has been studied. A method of treating spin waves in linear ferro- and antiferro-magnetic chains using semi-classical approximation has been developed. This work has now been extended to three dimensional lattice of magnetic systems.

1.5 *Electronic structure of atoms and molecules*

The electronic structures of conjugated organic molecules and the electron densities are extremely difficult to calculate by rigorous quantum mechanical methods. For molecules containing mobile electrons, the electron gas approximation was found more suitable. This method and its variations have been used to calculate the above mentioned properties of a large number of quinone molecules.

The study of correlation problem in some atoms and molecules using the modern many-body technique has been conducted for simple atom and molecules having π -electron systems.

1.6 *Mobility in polar semiconductors*

The transport properties of semiconductors are governed by the interaction of carriers of current (electrons and holes) with various other physical factors in the system such as phonons and static perturbing potentials. A general theory of mobility in compound semiconductors has been completed and a new concept of multi-band conduction has been introduced. The high and low temperature mobilities in compound semiconductors have been explained.

The behaviour of carriers in semiconductors in high electric fields has been studied. In the perturbation the role of the electric field causing intervalley or interband transition has been taken into consideration.

The resulting mobility has the form $\mu = \frac{A}{(B + CF^2)}$ where A, B and C are constants and F is applied electric field. This is in agreement with the observed mobility behaviour in systems such as GaAs etc.

1.7 *State of atoms in the presence of crystal and radiation fields*

The object is to study the spin and electronic states of paramagnetic atoms in crystals in the presence of the static and oscillating fields. By a suitable canonical transformation it was possible to get spin-spin interaction in some paramagnetic systems.

An expression has been derived for the temperature dependent exchange integral, for a pair of interacting shallow donors substituted in a dielectric material. This has been achieved by taking into account the phonon induced mixing of excited orbital states with the ground orbital states of the impurity centres. The results have been used to explain the temperature narrowing of the EPR line width observed by some workers in phosphorus doped germanium at low temperatures. Good agreement between theory and experimental results seems to favour the proposed mechanism in preference to one of motional narrowing due to hopping.

A new mechanism involving the transverse optical phonons and the spin system has been proposed. The transverse optical phonons couple directly with the spins owing to an effective magnetic field arising from such modes. The resulting expression gives a relaxation frequency in agreement with the experimental results on Cr^{+3} or Fe^{+2} doped magnesium oxide crystals.

1.8 *Magnetic break-down in solids*

The behaviour of matter in the presence of very high magnetic field has been studied to investigate the electron trajectories and the criteria of the magnetic break-down under various conditions.

The Schrödinger equation for certain typical electron orbits in metals was set up and the solutions of this equation were obtained. The probability that the adiabatic part is not followed, i. e. the criteria for the magnetic break-down was obtained by using the method of analytical continuation. It is found that high magnetic field low energy gap between two electronic states and a large bend in the adiabatic path, favours the phenomenon of magnetic break-down. Work on the problem has been completed.

RP.2 MATERIALS FOR SOLID STATE DEVICES

2.1 *Manganites*

New type of manganites having interesting semiconducting properties have been synthesized earlier which find applications as thermistor

material. It has also been established that ZnLi manganites show a new type of magnetic interaction under certain conditions.

On the basis of crystallographic and electrical studies of FeCuMnO_4 , CuCrMnO_4 and NiMnCrO_4 , it was found that these compounds exhibit the cubic spinel structure and Mn^{+4} and Cu^{+1} ions coexist in Cu-Mn spinels. Structural, magnetic and electrical studies of number of compounds having a general formula $\text{Cu}_x \text{Me}_{1-x} \text{Mn}_{2x} \text{Fe}_{2-2x}$ (where $\text{Me} = \text{Cu, Co, Ni, Mn}$ and Zn) have enabled to establish the site preference energies of the various transition metal ions for the octahedral and tetrahedral sites in the manganites containing Cu. The electrical conductivity measurements indicated that some of the compositions are suitable for low temperature thermistors.

Similar studies were carried out on $\text{ZnMn}_{2-x}\text{Ni}_x\text{O}_4$ systems. The paramagnetic susceptibility of these compounds confirmed our earlier observation regarding a new type of magnetic interaction in compounds containing Mn^{+3} and Mn^{+4} .

Thin film thermistors of manganites were prepared by chemical decomposition on glass substrate. Compositions with high temperature coefficient of conductivity (4%/degree) and small time constant have been developed.

Basic studies of the electrical and structural properties of manganites in the following three systems (1) $\text{Co}_x\text{Cu}_{1-x}(\text{Mn}_2)\text{O}_4$ (2) $\text{Mg}_x\text{Cu}_{1-x}(\text{Mn}_2)\text{O}_4$ (3) $\text{CuMn}(\text{MnNi})\text{O}_4$ are being conducted. Large number of samples have been prepared by sintering technique and the conductivity was measured at 1000 cycles. The activation energy data have been collected. Study of the hysteresis of conductivity has also been made.

2.2 Oxidic semiconductors

Semiconductivity of certain oxidic compounds has been studied and a correlation between their surface conductivity and catalytic activity established.

In plate-type zinc oxide crystals a resistance minimum and maximum was found at 325° and 370° respectively in air. The values shift to 300° and 390° in case of thin films doped with indium.

During the studies of D.C. conductivity of transition metal oxides, a persistent polarization was observed which was present even after the field was switched off. The polarization decayed according to the equation :

$$I_0 = I + I \exp -t/\tau$$

Further τ is found to be temperature dependent and follows the equation $\tau = \tau_0 \exp - \frac{\Delta E}{KT}$ where $\Delta E = \sigma$ Kcal/mole activation energy). A phenomenological theory has been developed for this behaviour which gives the relationship $I = I_0 \exp - t/\tau$ where $\tau = \Delta E_Q / 2 \pi \sigma$. The observed exponential dependance of τ on T suggests that σ varies as $\sigma = \sigma_0 \exp - \Delta E/KT$ indicating an activated mechanism of conduction. Hence this method can be used to determine the value of ΔE .

2.3 Thermoelectric semiconductors

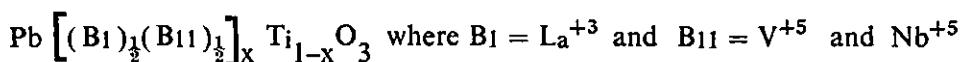
The thermoelectric figure of merit (Z) of a material is given by $\alpha^2/\rho K$ where α is the thermoelectric power, K is the thermal conductivity and ρ is the resistivity. In order to increase the efficiency of the system, some physical agencies which will increase α and decrease K and ρ have been introduced.

Measurement of Bi_2Te_3 , PbTe and their solid solutions have been carried out, and in many cases good thermoelectric properties have been observed.

Work on solid solutions of Bi_2Te_3 and Sb_2Te_3 which are suitable for thermoelectric generators, in high temperature region, is in progress.

2.4 Ferroelectric materials

Ferroelectric ceramics are widely employed as transducers for the generation of sonic and ultrasonic waves in electroacoustic pickups etc. Different samples of doped lead titanate of the general formula



were prepared. A detailed study of their structural and other characteristics in relation to their ferroelectric and allied properties has been undertaken.

Study of the above types of doped lead titanate samples (six compositions each for V and Nb by changing the value of X by 0.05) was continued. The spontaneous polarization, curie temperature and dielectric constants at different frequencies have been determined. It has been observed that samples doped with Nb shows better ferroelectric properties than that of vanadium samples. The curie temperature was decreased as the concentration of doping with V or Nb was increased. Dielectric constants have been determined from the hysteresis loops as well as by capacitance bridge measurements. The difference between the curie temperatures determined by capacitance bridge at 1 kc/s is always 10° - 40° higher than that determined from the hysteresis loops which may be ascribed as due to local heating at very high electric field

(21 kv/cm) applied to the samples in Sawyer-Tower circuit. The dielectric constants measured at room temperature at different frequencies (1 kc/s to 10 mc/s) showed that there was a decrease upto 1 mc/s, after that dielectric constant increased slowly.

2.5 *Photoconducting and electric properties of PbS*

The effect of internal oxidant on the various properties of chemically deposited PbS films has been systematically studied. It has been found that the addition of internal oxidant (H_2O_2) in the deposition bath improves the photoconducting properties of the films. The effect of oxidation treatment on PbS films was studied using the specially fabricated field effect bridge. It has been observed that the density of surface states of the thin film is strongly dependent on the duration of oxidation.

2.6 *Laser materials*

Recently, laser action has been observed in many Eu^{3+} chelates, particularly β -diketonates. These laser materials show a very strong fluorescence in the visible region particularly the transition ${}^5D_0 \rightarrow {}^7F_2$ which is supposed to lase, is very intense and has a narrow band width. A variety of new trivalent Eu, Sm and Tb chelates has been prepared. They include tris-(β -diketone) chelates complexed with bidentate ligands of the phenanthroline and dipyriddy types. Of particular interest is a broad class of anionic tetra tris-(β -diketone) derivatives which we believe to be eight-coordinate. Well resolved fluorescence emission spectra of all complexes are recorded. From this information an energy level structure for the lower states of the ground multiplet and excited states is obtained for the solutions.

Very recently laser action has been reported in some Nd^{3+} salts dissolved in selenium oxychloride in presence of stannic chloride at infra-red frequencies. An attempt has been made with Eu^{3+} , Tb^{3+} salts dissolved in an analogous compound like $SOCl_2$ in presence of stannic chloride.

2.7 *Metal-insulator-metal junctions*

Studies on metal-insulator-metal junctions are important in view of the recent developments in many thin film devices such as field effect transistors, negative resistance devices, oscillators etc. Metal-insulator-metal sandwiches using Al, Bi, Cd, Zn, Au, In etc. as electrode metal films and their oxide or sulphide films as insulators have been studied. In case of Al-CdS-Al-indium sandwiches it was found that after an irreversible break-down the I-V curve shows an interesting dual negative resistance phenomenon. When the upper

electrode is positive the curve first follows a low conductivity path from which it switches over to a high conductivity state through a current controlled negative resistance. On decreasing the voltage, the high conductivity path is maintained till a critical voltage in the opposite direction is reached when the structure switches back to the low conductivity state through a voltage controlled negative resistance.

RP.3 THIN FILMS

Properties of thin films (solid) often differ from the bulk material. Because of peculiar characteristic properties, thin films are finding wide applications in optical, semi-conducting, photo-conducting and other devices such as filters, rectifiers, resistors, capacitors, thin film transistors and thermistors photo-cells, detectors, sensors etc. These devices are finding greater uses particularly in space research, and micro-miniaturization. Since thin film properties are often structure sensitive, it is of great technological importance to make a systematic study of various thin films of elements, compounds or solid solutions both from the semiconducting and structural points of view.

3.1 *Structure of thin films*

A systematic electron diffraction study has been made on structures, crystal growth process, phase transition etc., of the vapour phase deposits in *vacuo* on different single crystal substrates of mica as well as on amorphous glass, at different substrate temperatures varying from room temperature to about 350°. The compounds studied were selenides and tellurides of mercury, indium, thallium as well as indium antimonide, which were prepared by mixing the elements in stoichiometric proportions, melting and cooling them in *vacuo*.

The study on the growth of HgSe and HgTe on different substrates showed that higher temperatures favoured the epitaxial growth of the deposits, whereas the deposition at the lower substrate temperature favoured the formation of polycrystalline deposits, with or without preferred orientations. On a (100) face of rocksalt, both HgSe and HgTe developed 2-d {100}, {111} orientations (normal as well as anti-type) and also 2-d {111} orientation of the crystallites rotated by 30°. Transmission patterns also indicated that in addition to the cubic phase, a hexagonal phase also developed both for HgSe and HgTe films. On a (110) face of rocksalt the deposits grew epitaxially with parallel orientations. On the (111) face, in addition to the normal cubic {111} orientation, 2-d {115} orientation of crystallites was also observed, no doubt due to the twinning on {111}. Similar orientation was also observed on mica cleavage faces.

Selenide and telluride of indium (In_2Se , In_2Te) which normally have orthorhombic structures (with lattice parameters $a=15.24 \text{ \AA}$, $b=12.32 \text{ \AA}$, $c=4.075 \text{ \AA}$ and $a=4.46 \text{ \AA}$, $b=12.62 \text{ \AA}$ and $c=15.35 \text{ \AA}$ respectively) grew epitaxially on all the faces of rocksalt as well as cleavage face of mica even though there were great dissimilarities on the disposition of atoms between the substrate and the deposits at the contact region. Often these developed on the cubic face of rocksalt, a new cubic phase in addition to the normal structure. For the new cubic phase a_0 was $\approx 5.4 \text{ \AA}$ for In_2Te . Both In_2Te and In_2Se crystallites grew epitaxially developing 2-d $\{001\}$ orientation on $\{100\}$ of rocksalt often rotated by 90° . On the (110) face of rocksalt also similar orientation was observed. On the (111) face, complicated patterns due to the formation of hexagonal crystallites were observed.

InSb developed 2-d $\{100\}$, $\{211\}$ orientation as well as 2-d $\{0001\}$ of hexagonal phase both rotated by 30° on the cube face of rocksalt. On the (111) face the deposits grew also epitaxially with 2-d $\{111\}$ along with $\{211\}$ orientation rotated by 60° . In case of mica cleavage face both the normal and anti-2-d $\{111\}$ orientations were observed along with extensive $\{111\}$ twinning, thus resulting in the appearance of 2-d $\{115\}$ orientation.

In_2Te_3 on the (100) face of rocksalt showed both cubic and hexagonal phases. Lattice parameters for cubic $a_0 = 6.15 \text{ \AA}$ and for the hexagonal phase are $a_0 \approx 4.35 \text{ \AA}$, $C_0 = 7.1 \text{ \AA}$. The crystallites grew epitaxially developing 2-d $\{111\}$ orientation along with a hexagonal phase with $\{001\}$ orientation rotated by 30° . On the mica cleavage face 2-d $\{111\}$ normal and antitype orientations developed.

Tl_2Se and Tl_2Te developed 2-d $\{001\}$ orientation when deposited on a (100) face of NaCl . The deposits developed a new $\{310\}$ twinned structure for the tetragonal lattice. Electron diffraction studies also revealed that Tl_2Te films also has a tetragonal unit cell with $a_0 = 8.88 \text{ \AA}$ and $C_0 = 13.20 \text{ \AA}$. These crystallites also developed $\{310\}$ type twinned structure.

3.2 *Physics of thin films*

Systematic study has also been made on the Hall effect, mobility, carrier concentration, mean free path of vacuum deposited films of the above compounds formed at room temperature as well as higher substrate temperatures. It has been found that Hall coefficients which were constant for the bulk materials were no longer constant for thin films, but increased with the increase of film thickness, with a tendency to attain a maximum value for thicker films; whilst remaining unchanged with impressed current and normally also with the magnetic field ranging between 2,000 to 7,000 gauss. Only in the

case of InSb films, R_H was found to be dependent on the magnetic field, however, decreasing with the increase of the field. It was also observed that it was only after annealing that InSb films showed considerable Hall effect. The higher substrate temperature of deposition had a pronounced effect in raising the R_H value of all the films and in the case of InSb films R_H increased by a factor of $\approx 10^3$ times than those deposited at room temperature. A simultaneous measurement of conductivity showed that this parameter also increased with substrate temperature. Hall mobilities for all the films were calculated and were found to increase with the film thickness as well as with the substrate temperature. μ_H as high as $3000 \text{ cm}^2/\text{v-sec.}$ was observed for InSb films deposited at about 350° of the substrate temperature. The majority carrier concentration was also determined for all the films, for different film thickness and substrate temperature. Similar was the case with meanfree path also. A comparison of the different semiconducting parameters of single crystal films of HgSe, HgTe and InSb compounds formed on freely cleaved mica substrate was made with those of polycrystalline films having more or less the same thickness and formed under similar conditions of evaporation. The single crystal nature of the films was confirmed by electron diffraction methods. Results show that R_H , σ , μ_H etc. increased considerably for single crystal films than for the polycrystalline, even though these values were much less than those obtained for the bulk material (single crystal).

The low values of the different semiconducting parameters for the films are explained on the basis of presence of some inter-grain boundaries, twin structures, voids, surface asperities etc. in the films in addition to the lattice defects present in them. The higher values of these parameters for films deposited at higher substrate temperature and also for single crystal films are, no doubt, due to their absence or removal during the deposition process.

A detailed study has also been made on resistivities, thermoelectric power, TCR etc. of SnSe, Sn_2Se_3 and SnS films. These films show two regions of slope for $\log R$ vs., $1/T$ curves. Films heated to higher temperature region showed irreversible change in the conductivity and the room temperature resistance was less as compared to that of unheated specimens. This appears to be due to a phase change of the specimen namely the change of the orthorhombic structure to the cubic one. The activation energy for these films were found to vary from 0.47 ev. to 0.51 ev. Here in these cases also, thinner films had higher ΔE compared to thicker films. Temperature of discontinuity (T_d) for all the films of SnSe, Sn_2Se_3 and SnS was 310° , 320° and 330° respectively. All the films were found to have much higher resistance ($1 \text{ M } \Omega$ to $\approx 100 \text{ M } \Omega$)-SnS films showed the maximum resistance. SnSe, Sn_2Se_3 and SnS films were found to be 'p' type semiconductors having thermoelectric power $\approx 155 \mu$ volts/ $^\circ\text{C}$, 160μ volts/ $^\circ\text{C}$ and 150μ volts/ $^\circ\text{C}$ respectively. Negative temperature

coefficient of resistance decreased with the rise of temperature and after reaching a minimum again increased with the further rise of temperature. This behaviour seems to be due to the contribution of the factor C/T^2 at higher temperatures in the expression for TCR. The temperature at which minima took place was dependent on film thickness. The shift of minimum on higher temperature side was for thin film.

SnTe films unlike SnSe, Sn_2Se_3 and SnS did not show any fall of resistance with increasing temperature in $\log R$ vs. $\frac{1}{T}$ curves. The curves, on the other hand, showed a slight increase of resistance with increasing temperature, suggesting a degenerate system similar to that of a metallic conductor. Low thermoelectric power ($\approx 42\mu$ volts/ $^\circ\text{C}$) independent of film thickness also confirmed the above view.

RP.4 CRYSTAL AND MOLECULAR STUDIES

4.1 Crystallography

Crystallographic studies of compounds reveal the molecular geometry and the nature of the intra- and intermolecular linkages, thus providing valuable data to understand the electronic properties of the molecules.

The structure of *p*-nitrobenzoic acid has been refined with the help of three-dimensional data. The molecular dimensions are compared with those of *p*-nitroaniline and *p*-nitrophenol; the variations are interpreted as being due to minor contributions from quinonoid valence-bond structures in the latter compounds.

o-Nitrobenzoic acid has been studied in detail and the bond lengths and angles have been obtained with an accuracy of $\pm 0.01\text{A}^\circ$ and $\pm 1\text{A}^\circ$ respectively. It has been found that due to intramolecular over-crowding the exocyclic carbon atom and the nitrogen atom move out of the aromatic plane in opposite directions. The structure has been compared with those of benzoic acid and *p*-nitrobenzoic acid.

In order to study the influence of an electron donor group substitution in para-position on the molecular dimensions of benzoic acid, the analysis of *p*-dimethylaminobenzoic acid has been undertaken. The compound crystallizes in the triclinic system; space group $\bar{P}1$, with two molecules unit cell of dimensions,

$$\begin{array}{lll} a=8.96 & b=7.97 & c=6.63 \text{ A}^\circ \\ \alpha=69^\circ & \beta=97^\circ & \gamma=94^\circ \end{array}$$

The molecules form dimers and are held in a stable structure by normal Van-der Waals interactions. The refinement of the structure is in progress.

The bond lengths and angles of 3,5-dichloroanthranilic acid have been determined with an accuracy of about $\pm 0.02 \text{ \AA}^\circ$ and $\pm 1 \text{ \AA}^\circ$ respectively. The molecule has been found to be slightly non-planar. The non-planarity of the molecule arises on account of intra- and intermolecular overcrowding.

In order to study the substitution in meta position of the benzoic acid molecule, structure analysis of *m*-aminobenzoic acid hydrochloride has been undertaken. Approximate structure has been determined and the refinement is in progress.

Sodium-2-oxocaproate crystals give a pattern of sharp and diffuse X-ray reflections. It has been shown that the crystals contain ordered, disordered polytypic regions in them. The type of disorder and the structure of the polytype are discussed and described.

Work on nickel-imidazole nitrate, potassium benzilate, *p*-nitrobenzaldehyde, and sodium salts of some α - keto acids is in progress.

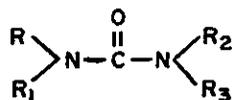
4.2 Spectrochemical studies

For quick characterization of compounds spectrophotometers equipped with fixed wave lengths (2-15 μ) are in use, but for detailed structural investigation instruments with high resolution must be employed. Work mentioned below is carried out on P. E. 221 infrared spectrometer fitted with NaCl-prism and grating interchange.

The infrared spectra of chalcones, flavones and isoflavones have been investigated with a view to understand certain anomalous results reported in the literature. Preliminary intensity measurements had shown that the main problem in these types of compounds arises from the fact that the C=C and C=O groups absorb in the same region and cannot be easily differentiated. Recently it has been shown that compounds containing a carbonyl group form weak complexes with I₂, BF₃ etc., and in these complexes the C=O frequency is shifted appreciably lower than the parent ketone making it possible to locate this absorption easily. Their studies with I₂ have shown that in 1, 6-dimethyl γ -pyrone the absorptions at 1678 cm⁻¹ is due to C=C stretching and the lower absorption at 1639 cm⁻¹ is the C=O bond. We recorded the spectra of chalcone, *o*-hydroxychalcone, flavone, 7-methoxy-5-hydroxyl and 3-hydroxyflavones, isoflavone, 7-methoxy-5-hydroxyisoflavones. Our studies showed, as would be expected, that the *o*-hydroxychalcone, the 5-OH flavone and isoflavone

are strongly hydrogen bonded but the 3-OH flavone (flavonal) is not. The hydrogen bonding in *o*-hydroxychalcone, 5-hydroxyflavone and isoflavone was so strong that the I₂ was not bound to C=O group. The anomaly in the reported values was due to the wrong assignment of the C=O absorption.

Infrared spectra of simple substituted ureas of the type



where R, R₁, R₂, R₃ = H or an alkyl group, have been investigated along with other deuterated derivatives to establish the various amide absorptions in these compounds. The coupling between the carbonyl and NH vibrations was also analysed.

In continuation of the work on alkoxy ethanols, monomer-dimer equilibrium in CCl₄ solution of the compounds C₂H₅OCH₂CH₂OH, C₁₈H₃₇OCH₂CH₂OH, C₂H₅OCH₂CH₂OCH₂CH₂OH & C₁₈H₃₇OCH₂CH₂OCH₂CH₂OH were studied by the IR spectroscopy in the hydroxyl stretching region. These compounds were found to form only dimers at higher concentrations in contrast to normal alcohols which form polymers at similar concentrations. In the case of compounds with two (OCH₂CH₂O) groups two types of intramolecularly bonded monomers having five and eight membered rings were found to be in equilibrium with the cyclic dimers.

For confirming the monomer-dimer equilibrium it was found essential to study the thermodynamic properties. In order to carry out such studies, a variable path length cell with heating arrangement has been fabricated. After testing for leak etc., the cell is now being calibrated.

Infrared spectra of nicotinic and isonicotinic acids were analysed and the frequencies due to NH⁺ and COOH groups have been characterized. Infrared spectrum of benzoic acid has been analysed by comparison with the spectra of its methyl ester, potassium benzoate, triphenylcarbinol and the deuterated products with attention focussed on the bands due to the alcoholic hydroxyl and carboxylic acid groups. Preliminary investigations on the infrared spectra of the first row transition metal complexes of the type M (Benzoate)₂ suggest that while both the hydroxyl and carboxyl groups are coordinated to Co (II), Ni (II), Mn (II) and Zn (II), Cu (II) shows coordination to both the carboxyl groups and only one hydroxyl group (of the two).

In continuation of the studies of aminobenzoic acids, a comparative study of the three forms of anthranilic acid was undertaken. While forms I and III are similar and probably dimers in the solid, form II is likely to consist of molecules which are dipolar. Further with the help of a variable temperature cell, it was found that form II changes over irreversibly to form I at 82°. Infrared spectrum of *p*-aminobenzoic acid was investigated and the assignments for the various bands were given.

RP.5 THERMODYNAMIC STUDIES

5.1 *Thermodynamic properties of solids*

Accurate measurements of the variation of specific heat of a solid with temperature often provide an insight into the details of its molecular structure, electronic energy level pattern, mechanism of various transitions and phase transformations, and also provide basic data for evaluation of thermodynamic functions, control or prediction of chemical behaviour.

Studies of heat capacities of the compounds of the type KMF_3 where $M = Mn, Co, Ni$ and Cu have been undertaken. Since the magnetic interaction in KMF_3 type of compounds is by superexchange, the random replacement of the transition metal by zinc may be expected to weaken the interaction, resulting in a lowering of the Neel temperature. The study of such an effect on $KNiF_3$ has been undertaken. Several compositions of $KNi_xZn_{(1-x)}F_3$ where $x = 0, 0.50, 0.69, 0.85$ and 1.0 have been prepared. The heat capacity measurements of them have been completed. It has been found that transition temperature is lowered as x decreases and no transition has been observed when $x = 0.50$ or less.

Thermal studies on $SrNi_{\frac{1}{2}}Co_{\frac{1}{2}}O_3$ and $SrW_{\frac{1}{2}}Ni_{\frac{1}{2}}O_3$ have been completed. The measurements on $SrW_{\frac{1}{2}}Co_{\frac{1}{2}}O_3$ are in progress. In continuation of the work on telluride systems, the heat capacity measurements on $Fe_{1.1}Te$ and $CrTe$ have been completed. These compounds show anti-ferromagnetic transitions.

Thermodynamic properties viz. entropy, enthalpy etc., have been evaluated for all the above compounds.

5.2 *Thermodynamic properties of solutions*

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

measurements in these solutions are expected to give interesting results. The adiabatic compressibility of dilute solutions of carboxy methyl cellulose has been determined from sound velocity and density data. The sound velocity was determined in an ultrasonic interferometer developed in the Laboratory. Assuming solvent molecules concerned in solvation to be effectively incompressible, the degree of solvation has been estimated from the adiabatic compressibilities of the solution and solvents. Adiabatic compressibility measurements of polymethacrylic acid (mol.wt. 7.9×10^5) at different degree of neutralization are being carried out.

5.3 *Thermodynamic properties of coordination compounds*

In the last few years, a thermodynamic study on the interaction of some transition metal ions with a number of aminoacids has been carried out with a view of examining the specificity shown by different ligands for various transition metal ions and identifying suitable ligands which can serve as chemical protective agents against radiation.

The thermodynamic quantities ΔF , ΔH and ΔS have been determined for the divalent transition metal ions Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} with the aminoacids cysteine and histidine in aqueous solution. The enthalpy changes accompanying the formation of histidine and cysteine complexes of the transition metal ions are nearly equal, but larger than the corresponding changes for the complexes of mono-amino-mono-carboxylic acids like α -alanine. The entropy changes for the formation of cysteine chelates are consistently larger than for the histidine chelates on account of greater coulombic interaction of the ligand with the central metal due to the presence of one more charged group in cysteine.

The higher value of ΔH and the lower value of ΔS accompanying the formation of *bis*-histidino Cu (II) chelate as compared to the corresponding changes in ΔH and ΔS values for the formation of *bis*-histidino chelates Zn (II), Ni (II), Co (II), Fe (II) and Mn (II) ions have been attributed to the tetragonal distortion of the octahedral symmetry of the ligand field around Cu (II) ion on account of Jahn-Teller effect.

RP.6 NUCLEAR AND RADIATION CHEMISTRY

6.1 *Effect of radiation on chemical reactions*

With the development of nuclear power programme it has become necessary to find uses for many by-products of this technology, one of which is gamma radiation. The possibility of using gamma radiation in promoting chemical reactions of industrial importance is being explored by us.

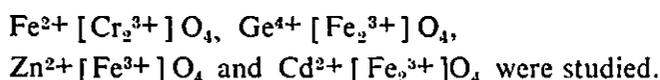
In the oxidation and amination studies of benzene a flow system at 300° was tried. In the case of amination of benzene to aniline, yields were better than those in the static system at 230°. For the hydroxylation of benzene, when water was replaced by methanol and ethanol (where the C-OH bond strength is considerably lower than the H-OH bond strength in water), a definite evidence of the occurrence of a chain reaction leading to phenol was obtained.

Methods of estimation of α - and β -naphthols produced in the oxidation of naphthalene, and of aniline and the three phenylene-diamines in the amination of benzene, were standardized, using *p*-nitrobenzene diazonium chloride as a coupling compound. For the final quantitative estimation of the products IR and visible spectrophotometers were used.

6.2 Mössbauer spectroscopy

6.2.1 *Mössbauer spectra of cubic ferrites with spinel structure* : Mössbauer spectroscopy has been used to study cation oxidation state and site distribution in mixed oxide system where cations have a variable valency and can occupy more than one possible non-equivalent site.

Mössbauer spectra of



Mössbauer spectra of the spinels, $\text{Fe}(\text{CoNi})\text{O}_4$ and $\text{Fe}(\text{MnCu})\text{O}_4$, which contain Fe^{3+} at the A sites, show a pronounced quadrupole splitting of 0.4 mm/sec. at 465° and 0.5 mm/sec. at 454° respectively in their paramagnetic states. This may be attributed to the asymmetric charge distribution associated with the random distribution of the trivalent and divalent ions on the neighbouring twelve B sites which surround each A site.

The Mössbauer spectra of the above spinels at room temperature, when they are in their ferrimagnetic states, show hyperfine splitting but no quadrupole splitting. The observed well separated doublet in the spectra of $\text{Fe} [\text{CrNi}] \text{O}_4$ and $\text{Fe} [\text{MnCu}] \text{O}_4$ in the paramagnetic state indicates the presence of an Electric Field Gradient (EFG). The quadrupole splitting ΔE_Q , in the presence of an axially symmetric EFG tensor with the symmetry axis at an angle θ with respect to the magnetic axis, is given by the expression

$$\Delta E_Q = \frac{e^2 q Q}{4I(2I-1)} [3m^2 - I(I+1)] [3\cos^2\theta - 1] \\ \text{for } I = 3/2, \quad \Delta E_Q = \frac{e^2 q Q}{4} [3\cos^2\theta - 1]$$

If therefore, the magnetic field H is inclined at an angle $\theta = \cos^{-1} \frac{1}{\sqrt{3}}$ to the symmetry axis of the EFG, the hyperfine spectrum in the magnetic state would not show any quadrupole splitting.

6.2.2. *A Mössbauer study of the nature of bonding in $Fe^{3+}(acac)_2Cl$ and $Fe^{3+}(acac)_2Cl_2$.* Mössbauer spectroscopy has also been used to explain the nature of chemical bonding of some organometallic compounds. The Mössbauer spectrum of $Fe(acac)Cl$ shows no evidence of quadrupole splitting while the Mössbauer spectrum of $Fe(acac)Cl_2$ shows a quadrupole splitting of 0.44 mm/sec. at -194° . The unsplit resonance line in the spectrum of $Fe(acac)_2Cl$ indicates that Fe^{3+} ion is bound to four oxygen atoms from the two acetylacetonate ions and that the Cl -ion is outside the coordination sphere. The isomer shifts of both these compounds show that the iron-oxygen bonds are predominantly ionic. This result is in agreement with the observed magnetic moment of 6 Bohr Magnetons for the above two compounds.

6.3 Diffusion in solid state

Studies on intermetallic diffusion provide valuable data on mobility of atoms at high temperatures. As part of a long range programme, diffusion of fission products in aluminium was studied. Values of diffusion coefficient for Ag^{110m} in aluminium were reported earlier.

Diffusion of antimony (Sb^{125}) in aluminium has been studied in the temperature range $450-630^\circ$ by means of residual activity method. The value of diffusion coefficient is given by the equation :

$$D = 0.0881 \left[\frac{-29076}{RT} \right] \text{ cm}^2 | \text{ sec.}$$

$$Q = 29.076 \pm 0.369 \text{ Kcal} | \text{ mole}$$

$$D_0 = 0.0881 \pm 0.02 \text{ cm}^2 | \text{ sec.}$$

RP.7 CATALYSIS

7.1 Nickel-Zinc catalysts

Using different proportions of nickel and zinc, a series of catalyst compositions were prepared in the form of mixed oxalates by co-precipitation. The decomposition temperatures and surface activities of the catalysts were studied

by thermogravimetric analysis and surface area determinations. These studies have shown that the two oxalates form a homogeneous solid solution, which has been confirmed by X-ray studies. The activation energies for decomposition and reductions have been evaluated.

7.2 Vanadium pentoxide catalyst

The pentoxide was prepared by thermal decomposition of ammonium vanadate. Thermogravimetric analysis revealed that the decomposition proceeds in four well-defined stages. Analysis of the various intermediates and their surface area measurements showed that they possess low surface areas, whereas the supported V_2O_5 catalyst showed much larger surface areas which decreased on further heating to 500°.

7.3 Copper promoted nickel catalyst

Basic studies of the promoter action of copper on the catalytic properties of nickel showed that the interpenetrating gel structure of mixed nickel and copper carbonates lower the bulk density and enhances the surface area. It also retards considerably the rate of sintering of the mixed oxides (and the mixed metals) obtained from the co-precipitated carbonates.

The use of conventional inert supports, such as pumice, kieselguhr, carbon and alumina, was also investigated for the nickel copper catalyst. However, contrary to expectation, the activity of the supported catalysts was found to be somewhat less than that of the unsupported ones. This is probably due to the dependence of activity on only the physical surface area of the catalyst particles in the liquid phase hydrogenation of vegetable oils. The increase in surface area provided inside the bulk of the support appears to be inaccessible to the big molecules of fatty acid glycerides.

The influence of addition of copper (as mixed formate) on the activity of the nickel formate catalyst was also investigated. In this system, however, copper did not show any promoter action. In fact, the mixed nickel-copper catalysts obtained from mixed formates were found to be somewhat less active than the catalysts obtained from nickel formate alone.

The study of the cobalt-nickel mixed formate system also did not show any improvement in activity.

7.4 Thin films of copper

In experiments with vacuum-deposited copper film, it was found that the film does not adsorb molecular hydrogen at low temperatures. However,

atomic hydrogen is taken up rapidly at liquid air temperatures. On raising the temperature the hydrogen atoms recombine and desorb as molecular hydrogen.

RP.8 SYNTHETIC INORGANIC CHEMISTRY

8.1 *Titanium organics*

India being one of the richest countries in the world in titanium resources, a study of its chemistry and of technological applications of its compounds has been on the research programme of the NCL for some time. Lately, this study has been extended to include titanium organics. In the last fifteen to twenty years there has been a spurt of publications on the applications of organic titanium compounds as heat-resistant surface coatings, waterproofing compositions, cross-linking agents and especially as polymerization catalysts.

A survey of the literature during the period shows, however, that though certain areas covering industrial applications have been under intensive research, a systematic covalent chemistry of titanium is still to be developed. Difficulties arise because of the frequently polymeric nature of the products, and there similarities as well as notable differences in the organic chemistry of the two elements, silicon and titanium.

Starting from the commercial chemical, titanium tetrachloride, some results on the synthesis of new titanium organics in which the organic moieties are linked non-ionogenically through oxygen were communicated in the last year's report. While the work was continued in synthesizing other typical groups of organoxytitanium compounds, special interest was associated this year with the observed increased stability of sigma-bonded Ti-C type of organics prepared from titanium chelates. Starting with di- or trichloro titanium (IV) derivatives of some bidentate chelates, the lithium phenyl reaction gave rise to compounds of the type $\text{Ph}_{4-x}\text{TiL}_x$ (LH = bidentate ligand such as salicylaldehyde, dibenzoyl methane etc., and $x = 1$ or 2), provided that the phenylating reagent did not react with the ligand itself. The new compounds give definite melting points, respond to the mercuric chloride test for Ti-C bond, and some are stable enough to show their monomeric nature in boiling benzene. Selected compounds are to be examined further for possible applications.

Cyclohexanol, though it shows some obvious similarities with aliphatic alcohols in its orthotitanate ester, has a different stereochemistry of its own, which would be expected to give rise to properties of its titanium compounds different from the aliphatic and aromatic hydroxy derivatives of titanium. The isolation of mono- and dichloro cyclohexanoxy-titaniums provided easy

routes to the synthesis of a number of cyclohexanoxo-titaniums linked to various ligands, including chelates. In some cases of substitution reactions with the cyclohexanoxides, however, the cyclohexanoxo group was knocked out forming Ti-O-Ti chain, in analogy with similar behaviour of the alkoxides.

Further reactions of some of the chloro intermediates, reported last year, were continued. The mono-substituted intermediate $(L)TiCl_3$ (where $LH =$ phenol, salicylaldehyde, methyl salicylate) was reacted with hydroxylic compounds and chelates. Ethanol gave derivatives of the type $(L)(C_2H_5O)TiCl_2$. C_2H_5OH ; phenol and catechol replaced all the chlorine atoms giving $(L)Ti(OC_6H_5)_3$ and $(L)Ti(O_2C_6H_4)(OC_6H_4OH)$ respectively. Salicylaldehyde and methyl salicylate replaced one chlorine only forming the dichlorides $(L)(\text{salicylaldehyde/methylsalicylate})TiCl_2$, whereas acetylacetone replaced two chlorines forming the monochlorides $(L)(\text{acetylaceton})_2TiCl$. Acetylacetone also reacted with $(L)_2TiCl_2$ ($LH =$ salicylaldehyde, methyl salicylate) giving monochlorides $(L)_2(\text{acetylaceton})TiCl$.

A number of the newly synthesized titanium compounds showed marked water-repellency, but so far their effects have been found to be less persistent than that of the well-known organo-silicon compounds.

8.2 Coordination polymers

Titanium tetrachloride or titanium tetrabutoxide, dimethyl tin dichloride and zirconium oxychloride on reaction with *bis*-(8-hydroxy-5-quinolyl) methane and on partial hydrolysis afford the coordination polymers whose compositions were determined on the basis of elemental analysis. The infrared spectra and TGA of these polymers obtained as insoluble powders were recorded. The reaction between dichloro *bis*-(2,4-pentanedione) titanium and the above *bis*-ligand yielded a reddish-brown polymeric material containing chlorine. Diethoxy-, diisopropoxy and dibutoxy *bis*-(8-quinolinolato) titanium compounds also gave on partial hydrolysis *bis*-(8-quinolinolato) titanoxane polymers whose IR spectra showed strong and very broad absorption bands at ca. 820 cm^{-1} and ca. 730 cm^{-1} , presumably due to the presence of Ti-O-Ti bonds.

The compositions and thermogravimetric decompositions of the coordination polymers of Cu (II), Ni (II) and Co (II) with resorcinol-2,4-dialdehyde have also been determined.

8.3 Spectral studies of coordination compounds

Electronic absorption spectra of copper chelates of β -dicarbonyl compounds : Close similarity of the ultraviolet and visible spectral bands of copper chelates

of β -diketones, β -ketoester, β -ketoamide and β -ketoanilides has been shown as evidence of a common structural pattern for all these chelates. It has been brought out that no relation exists between the position of an ultraviolet spectral band and the stability of the metal chelates. The visible spectral band of the chelates showed appreciable red shift with increasing coordinating power of the solvents used. This has been explained from the view point of crystal field-ligand field theory as due to adduct formation with the solvents. Different degrees of intensification of the visible band of metal chelates in pyridine have been shown as arising from different adduct ratios; 1:1 ratio leading to an acentric square pyramidal structure (hence the high intensity) and 1:2 ratio to a centric hexacoordinate structure (low intensity).

8.4. *Infrared absorption spectra of metal chelates of acetoacetanilide*

References to the chelates of acetoacetanilide are few in the chemical literature. Chelates of Be (II), Al (III), Cr (III) and Fe (III) were synthesized for the first time. Acetoacetanilide and some of its metal chelates were deuterated to establish various hydrogen modes of vibrations in these compounds and the hydrogen bonding behaviour of the ligand in solution. The salient features of the infrared spectra of acetoacetanilide and those of its chelates with metals like Cu(II), Be (II), Al(III), Cr (III) and Fe (III) have been brought out by a comparative study.

8.5 *Coordination compounds : their reactivity and isomerism*

Since the industrial potential of coordination compounds is promising, work in this field is being pursued (with a view to study their reactivity and structural characteristics for the present). The preparation of new compounds and investigations on new reactions are the main purposes of this basic research which may lead in future to a study of their possible applications.

During the course of studies on the reactivity of chelated ligands reported last year, the possibility of mercuration in some chelated β -dicarbonyl compounds has been examined. Organomercury compounds viz. diacetoxymercuri acetylacetone, diacetoxymercuri trifluoroacetylacetone, diacetoxymercuri ethylacetoacetate, diacetoxymercuri acetoacetanilide and diacetoxymercuri *o*-chloroacetoacetanilide have been prepared by reacting the respective metal β -dicarbonyl chelated compounds with aqueous mercuric acetate. In all the compounds prepared, mercury retains its salt-forming character and splits off easily when treated with H_2S , HCl , KI , hydrazine hydrate or phenyl hydrazine, indicating a weak mercury-carbon linkage.

8.5.1 *Ligand replacement in metal acetylacetonates by ethylenediamine tetra-acetic acid* : Solid EDTA chelates of metals are usually prepared by using simple metal salts and alkali or ammonium salts of EDTA. Possibilities of anion penetration leave in doubt the exact composition of the products thus obtained. Several metal acetylacetonates were found in this investigation to react with EDTA in aqueous suspension. From the resulting solution, well-defined crystals of metal-EDTA chelates have been isolated. The EDTA chelates prepared by ligand replacement are of copper (II), nickel (II), cerium (III), lanthanum (III), neodymium (III), zirconium (IV) and thorium (IV). The best use of this method however, has been in the preparation of manganese (III) chelate of EDTA. EDTA chelate of Ti (IV) was also prepared. Infrared spectra of these chelates have been compared.

8.5.2 *Titanium complexes of acetoacetanilide* : Monochloro- and dichloro-acetoacetanilide complexes of titanium have been reported earlier (paper 39). Subsequently, monochloro-*tris*-(4-anilido-2,4-butanediono)titanium (IV) was also prepared by an entirely different route, via the isolation of an addition compound of $TiCl_4$ with three molecules of the ligand and subsequent heat treatment of the addition compound. Monobromo- and moniodo-*tris*-(4-anilido-2,4-butanediono)titanium (IV) complexes were also isolated for the first time. The moniodo complex, however, was found to have one solvated molecule of hydrogen iodide. TGA data also revealed that the moniodo compound is different from its chloro or bromo analogues. It loses HI before rapid decomposition of the chelate starts. Trichloromono-(4-anilido-2,4-butanediono)titanium (IV) was also isolated and its reactions with organometallic compounds are under study.

8.5.3. *Isomerism of tris-(acetoacetanilido)-chromium (III)* : Two possible geometrical isomers of *tris*-(acetoacetanilido)-chromium (III) were studied. It was found that there is a significant difference between these two isomers, the *trans*-compound being thermally more stable than the corresponding *cis*-compound. A report on this has been published (paper 40).

8.5.4. *The nature of uranyl chelates of acetoacetanilide and ortho chloro-acetoacetanilide* : The urge for increased coordination number for uranium finds expression in the two new uranyl complexes isolated. These complexes of UO_2^{++} with acetoacetanilide and acetoacetortho-chloroanilide contain an extra molecule of the ligand which perhaps occupies only one coordination position. A comparison of the IR spectra of these complexes with those of their copper and chromium analogues revealed the nature of attachment of the extra molecule of the ligand. Although TGA data revealed that the extra ligand molecule is knocked off sharply, isolation of complexes free of the extra molecule was not successful owing to their instability.

8.6 Fluorine chemistry

A hydrofluoric acid industry is now being set up in the country. This forms the basis for the manufacture of industrially important fluorine chemicals such as the Freon refrigerants, fire retardants, aerosol propellents, fluorocarbon resins, plastics, lubricants and also synthetic cryolite and aluminium fluoride required in aluminium metallurgy.

The preparation and study of some organic fluorine compounds by different methods have been undertaken. Starting from benzotrifluoride and through the corresponding hydrazine, a CF_3 substituted dithizone was prepared. Uses of this compound as an analytical reagent are being studied.

A micro-analytical apparatus for the estimations of C and H in organic fluorine compounds has been set up. A cell for electrochemical fluorination of organic compounds has been fabricated.

RP.9. PHYSICO ANALYTICAL CHEMISTRY

9.1 *New reactions of analytical importance*

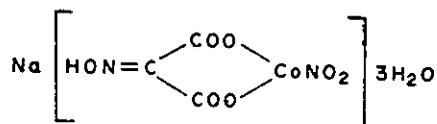
Efficient analytical service inevitably involves original investigations in the laboratory connected with the type of samples which the group is called upon to examine. The following investigations have been carried out in this connection.

9.1.1. *Direct reduction of insoluble vat dyes in the solid state at the dropping mercury electrode* : Direct reduction of vat dyes held in suspension at the dropping mercury electrode gave rise to peaks at characteristic potentials. The peak currents, however, were found to depend on several parameters such as particle size, rate of stirring etc.

Comparison of half-wave potentials of certain vat dyes with their respective peak potentials does not show any simple thermodynamic relationship. Nevertheless the respective peak potentials can be used for the qualitative identification of such vat dyes which are polarographically active in the solid form. (paper 51)

9.1.2. *Separation and electro-depositions of Ni and Co* : The accurate determination of Ni and Co from their mixtures by using conventional gravimetric or titrimetric procedures involves prior separation of one from the other. Even a good method for cobalt, viz., electrodeposition at the cathode, suffers from serious limitations. A new method for the ion

exchange separation of cobalt from nickel, followed by electrodeposition of cobalt from a malonate solution, has been developed. It is based on our observation that cobalt reacts with malonic acid in presence of sodium nitrite to give an anionic complex carrying a single negative charge, whereas nickel under similar conditions gives a neutral complex. Further investigation of this reaction has led to the isolation of a new cobalt (II) complex salt which may be formulated as :



Partial success has been achieved also in the electrodeposition of cobalt alone in presence of both cobalt and nickel from ammoniacal bath containing perchlorate, nitrate and malonate. During the course of this investigation, a complex nickel ammonium perchlorate salt having the composition $\text{Ni}(\text{NH}_3)_5(\text{ClO}_4)_3$ has been isolated.

9.1.3. *Mechanism of the molybdate dimethylglyoxime reaction* : In the molybdate catalysed reduction of dimethylglyoxime with stannous chloride to ammonia, diacetyl and acetoin, spectrophotometric and polarographic evidence supports the view that Mo (III) and/or Mo (IV) is the catalytically active species. It is interesting that even in the absence of stannous chloride, the molybdate ion catalyses reduction of dimethylglyoxime at the dropping mercury electrode. This is inferred from the enhanced limiting currents obtained for the Mo (V) — Mo (III) polarographic step in presence of dimethylglyoxime.

RP.10 NATURAL ORGANIC PRODUCTS

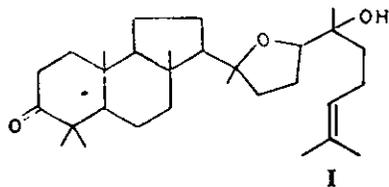
10.1 *Cedrela toona* (Hin. : Tun)

The work has been undertaken to study the chemistry of extractives from commercially important Indian timbers. From the non-volatile portion a new degraded triterpene similar to cederolone was isolated.

Geranylgeraniol, the biogenetic precursor of diterpenoids and carotenoids, has been identified as one of the components. Isolation of this precursor from a natural source is being reported for the first time. Geranylgeraniol has been found to occur both in the free state as well as esterified with long chain fatty acids.

10.2 *Ailanthus malabarica* resin (Mal. : Mattipal)

Work on this indigenous forest product was initiated with a view to study its chemistry for assessing its commercial utility. The resin consists of several triterpenoids which have been found to belong to an entirely new class of triterpenoids. The structure of the major component has been deduced to be (I).



10.3 *Boswellia serrata* (Hin. : Salai)

Salai gum is a regular forest product of Madhya Pradesh and its annual potential is around 350-400 T/annum. Work on this gum was initiated with a view to study its chemistry for assessing its commercial utility in newer fields. The gum was separated into acidic and neutral components and the former was found to consist of β -boswellic acid.

The neutral part of the resin was examined and three new triterpenes isolated and one being identified. A quantity of essential oil of the gum has also been collected for further studies.

10.4 *Terminalia tomentosa* Gum (Mar. : Ain)

The presence of D-galactose, D-xylose, L-arabinose, L-ramnose and D-glucuronic acids in the gum was mentioned in the previous report.

Partial degradation of the gum followed by chromatography gave two aldobiouronic acids which were assigned the following structures :

- (1) 3-*o*-(β -D-glucopyranosyluronic acid)-D-galactose
- (2) 4-*o*-(β -D-glucopyranosyluronic acid)-D-galactose

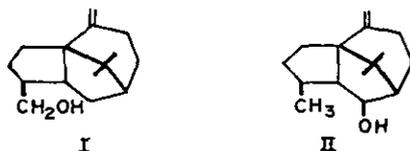
10.5 Stereochemistry of Nimbin

After finalising the structure and stereochemistry of nimbin, the main crystalline bitter constituent of neem, its absolute stereochemistry has been determined by measuring the Optical Rotatory Dispersion curve of pyronimbinic acid mesylate a diene derivative of nimbin. (paper 69)

10.6 *Cyperus scariosus* (Mar. : Nagarmutha)

The oil from the roots of this plant is available in the country and is used for perfumery and medicinal purposes. The chemical constituents of this oil are being studied.

The isolation of a new crystalline sesquiterpenic ketone, isopatchoulenone, from the ketonic fraction of the oil was reported earlier. From the ether fraction of the oil three alcohols have been isolated in pure form and out of these, structures and absolute configurations for a primary (I) and a secondary alcohol (II) have been determined. They have the same basic skeleton as the ketone isolated from the oil.

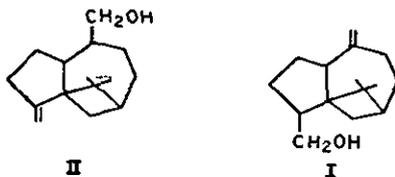


10.7 *Vetiveria zizanioides* (Hin. : Khus)

Khus is a well-known perfumery oil commercially produced in the country from the plant, *Vetiveria zizanioides* . In South India (Kerala and Madras), oil is obtained from the roots of the cultivated variety, while in North India (Bharatpur, Musanagar etc.) it is obtained from the roots of grass which grows wild. The North-Indian variety of the oil is laevo-rotatory and South Indian variety is dextro-rotatory. Chemical compositions of these two oils are also quite different. It is gathered that khus oil worth Rs. 3 lakhs is exported every year and a similar quantity is consumed in the country for the manufacture of different perfumery products.

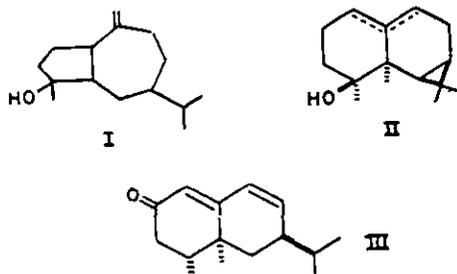
Studies on North Indian variety have been reported last year. The chemical composition of the South Indian variety is now being studied in detail. With the help of GLC and TLC analysis it has been shown to be a complex mixture of at least 30 components.

Four monoterpene hydrocarbons have been identified as α -pinene, limonene, *p*-cymene and Δ^3 -carene. Ten sesquiterpenes have been isolated in the pure form. A new tricyclic sesquiterpene primary alcohol khusimol, $C_{15}H_{24}O$, has been isolated from South Indian vetiver oil. It has been assigned structure (I). Further examination of the alcohol fraction of the oil has led to the isolation of another primary alcohol, $C_{15}H_{24}O$, having the same carbon skeleton as in Khusimol. It is proposed to name it as isokhusimol and the structure II has been assigned to it. The ketone fraction (isolated in the form of semicarbazone derivatives) was found to contain a mixture of about six ketones from which a solid ketone and α -vetivone have been isolated.



10.8 *Nardostachys jatamansi* DC (Hin. : Nard)

This is a reputed medicinal plant described in Ayurvedic literature. Essential oil was extracted from the powdered roots of the plant by low temperature solvent extraction method (yield 4.3 %). Investigation on this plant of Indian origin has led to the isolation of three new sesquiterpenoids nardol (I), calarenol (II) and nardostachone (III), along with some known sesquiterpenic compounds such as calarene, valeranone and valeranal. Several aliphatic compounds, isovaleric acid, n-hexacosanyl arachidate, n-hexacosane, n-hexacosanyl isovalerate and n-hexacosanol were also isolated and characterized along with the steroid β -sitosterol.



10.9 *Saussurea lappa* Clarke (Costus roots-Kashmir & Punjab varieties)

The costus plant is a typical valuable Indian raw material which grows mainly in Kashmir and the hill districts of Punjab at high altitudes. The annual production of roots is estimated to be 560 Tonnes. A low temperature solvent extraction procedure has been developed to obtain the oil in its natural form without any denaturing and polymerization. This oil is acceptable in perfumery and so far oil worth Rs. 70,000/- has been exported during the last few years.

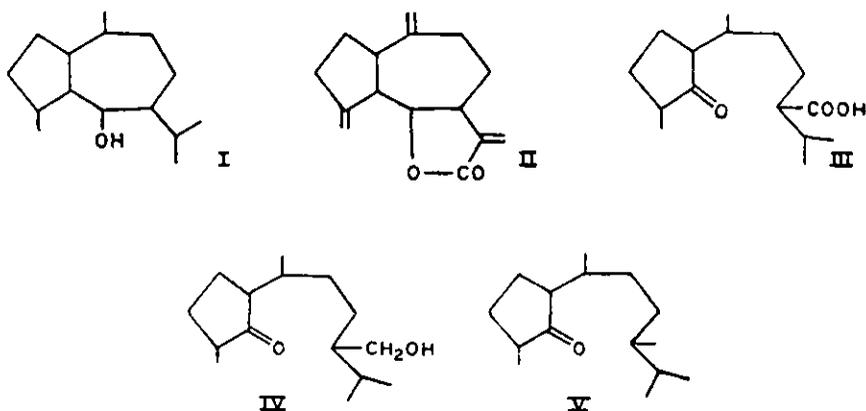
Costunolide, dehydrocostus lactone and costic acid are some of the important constituents of the oil. The structure, stereochemistry and some interesting transformations of these constituents have been studied.

10.9.1 *Dehydrocostus lactone*: The structure of dehydrocostus lactone suggested by Sorm has been rigourously established by chemical evidences. A ketocarboxylic acid obtained during CrO_3 oxidation of the monol (I) obtained from dehydrocostus lactone (II) was assigned structure (III) on the basis of bromination and dehydrobromination experiments. Additional evidence has now been obtained by showing the presence of cyclopentanone absorption in (III) by initially converting its ethylene ketal into the corresponding alcohol by LAH and regenerating the ketol (IV) from it. The ketol has also been converted into the ketone (V). This conclusively proved the structure of the keto acid (III) and also established the presence of a cyclopentane ring in dehydrocostus lactone.

Dehydrocostus lactone on treatment with formic acid gave a solid in which one of the two isolated exocyclic double bonds appears to have migrated inside the ring and a formate group is also introduced in the molecule. Further evidence in connection with its structure is being collected.

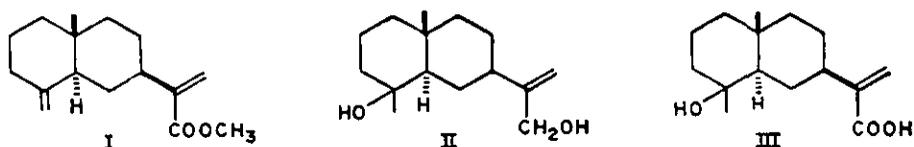
Chamazulene which occurs in chamomile oil, possesses anti-phlogistic and anti-allergic properties. Since it is not available in quantity at a reasonable cost, a closely related product, guaiazulene, is widely used in cosmetics. With the easy availability of dehydrocostus lactone from costus root oil, it is now possible to explore its conversion into chamazulene.

It has been found that dehydrogenation of the derivatives of dehydrocostus lactone by conventional methods using sulphur and selenium gives azulenes in low yields. A new procedure, involving treatment of the derivatives with alkali at high temperatures in suitable solvents is being explored.



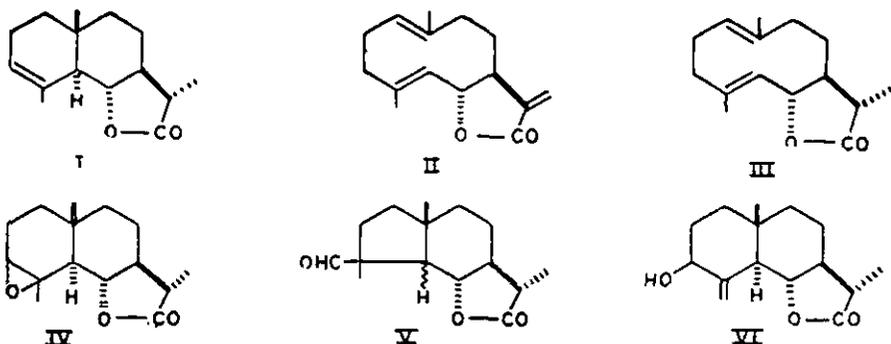
10.9.2 *Costic acid* : The structure and stereochemistry of costic acid have been well established, and its conversion into other naturally occurring eudesmane-type compounds has been undertaken.

Methyl ester (I) of costic acid has been converted into its monoepoxide which has been reduced to the diol (II) by AlH_3 . The diol was oxidized by Jones reagent to the corresponding conjugated aldehyde and subsequently to the acid (III). The latter is under examination.



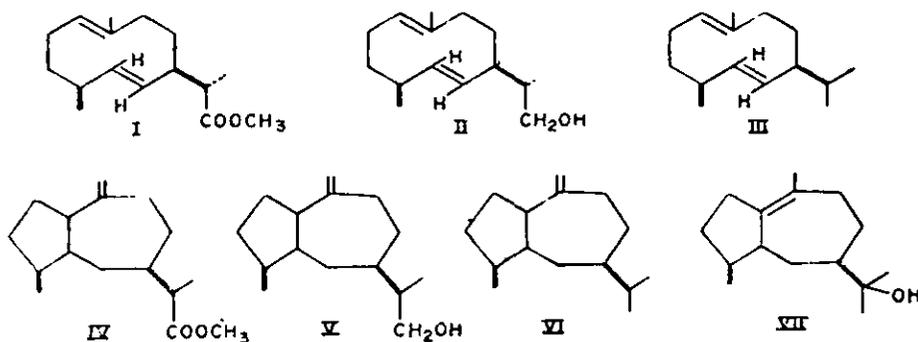
10.9.3 *Conversion of costunolide into eudesmane-type compounds* : Attempts are being made to convert costunolide into α - and β -tetrahydrosantonins and also to santonin.

α -Cyclo-dihydrocostunolide (I) obtainable from costunolide (II), and also from solid dihydrocostunolide (III) was converted into its epoxide (IV) and the latter subjected to acetolysis to give a ring contracted compound (V) and presumably a hydroxy lactone (VI). Characterization and structure determination of (VI) are in progress.



10.9.4 *Transformation products of costunolide* : Thermal rearrangement of cyclodeca-1,6-diene system, obtainable from costunolide, to a guaiane system is being studied.

The thermal rearrangement of the ester (I), alcohol (II) and hydrocarbon (III) obtainable from costunolide as such and also in presence of diethylene glycol and alkali has been studied. They rearrange to the corresponding guaiane type of compounds (IV), (V), (VI) for which chemical evidence has been obtained. The compounds containing exocyclic double bonds have been observed to undergo rearrangement to bulnesol type (VII) of compounds on treatment with an acid.

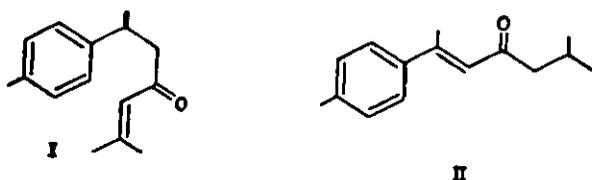


10.10 *Curcuma longa*, Turmeric (Hin. : Haldi)

Turmeric is cultivated in India as a widely accepted spice. Nearly 3000 Tonnes of turmeric are annually exported, valued at Rs. 1 crore. Besides as a spice, turmeric is valued for its colouring material curcumin and the flavouring essential oil. Turmeric oil is commercially produced in the country.

The chemistry of turmeric oil was studied in detail. It was found that turmeric oil consists of turmerone and ar-turmerone as its main constituents, and turmerone can be converted to ar-turmerone. Recently, interest in evaluating the flavouring qualities of ar-turmerone has been shown by a foreign firm to whom a sample has been sent. Simultaneous efforts are being made to standardize the efficient conversion of turmerone to ar-turmerone.

In the fundamental studies, a number of optically active indanes of known absolute configurations were prepared starting from ar-turmerone. New methods have been developed for the synthesis of ar-turmerone (I). An isomeric ketone (II) has also been synthesized. The cyclization reaction of a number of compounds related to ar-turmerone has been carried out.



10.11 Analysis of solvent extracted sandalwood oil

CFTRI, Mysore, are developing a process for the extraction of sandalwood oil by solvent extraction. In order to evaluate the solvent extracted sandalwood oil the volatile constituents of the oil were studied. It was found that the oil consists mainly of α - and β -santalenes and α - and β -santalols. During the course of investigations, it was possible to obtain a mixture of α - and β -santalols free from hydrocarbons and colouring material. The results and the respective samples have been sent to CFTRI.

10.12 *Inula racemosa* (Kashmir : Poshkar)

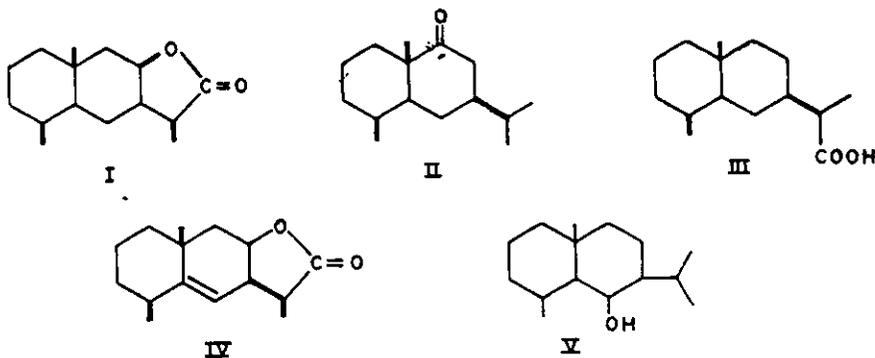
Inula racemosa is a stout herb found in north Himalayan region at altitudes of 5000 to 14000 ft. The roots have strong odour resembling camphor. They contain an essential oil (yield 6%) which consists of more than 50% of lactone mixtures (alantolactone and isosalantolactone).

Alantolactone is known to possess strong anthelmintic properties and is more potent and less toxic than santonin.

The lactones isolated from this source are found related to lactones isolated from the costus root oil. The chemistry and structural transformations of alantolactones have been studied and it was possible to synthesize 9-keto-eudesman (dihydrocanarone) (II) and tetrahydrocostic acid (III) from tetrahydroalantolactone (I). Compounds (II) and (III) have already been isolated from other natural sources. The intermediate products in above transformations have been characterized and their stereochemistry established.

On similar lines, transformation reactions of dihydroalantolactone (IV) have been carried out to synthesize dihydro-junenol (V), a constituent of North Indian vetiver oil.

In view of the potential pharmaceutical importance of alantolactone, efforts are being made to standardize its isolation from the oil. The biological activity of isoalantolactone will also be tested.



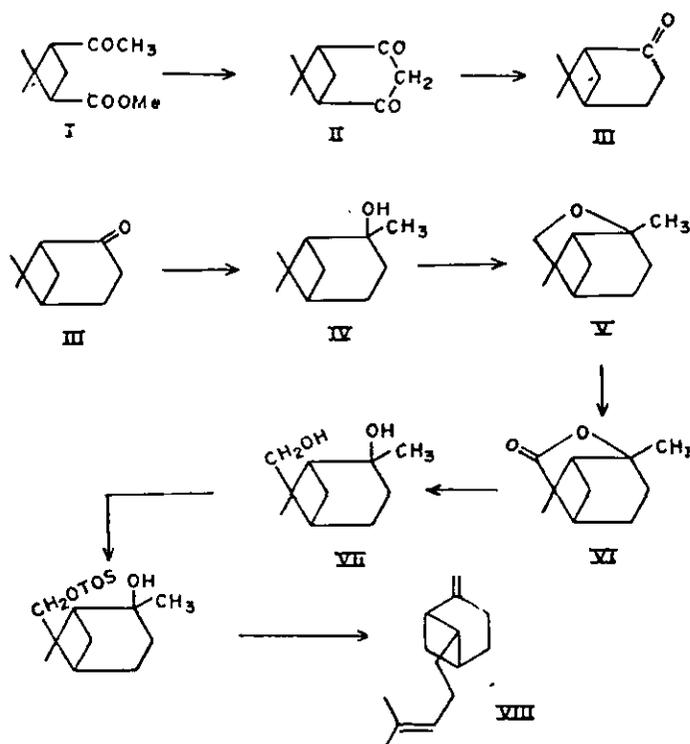
10.13 Valerian root oil and synthesis of bergamotenes

The plant *Valeriana wallichii* is widely grown in the temperate Himalayas at varied altitudes of 4,000-10,000 ft. The volatile root oil is used in perfumery and in indigenous medicine. It has a depressant effect upon the central nervous system. The systematic investigation of the various constituents of the oil was conducted and it was found to contain valeranone, β -sitosterol maaliol, β -patchoulene, α -curcumene, calarene, patchouli alcohol, β -bergamotene and hydroxy-valeranone in the neutral portion. The acidic portion contains mainly isovaleric acid and β -methyl-n-valeric acid. The structures of these compounds have been fully elucidated.

It was found that β -bergamotene is a pinene analogue, and hence attempts are being made to synthesize the same. Based on the known synthesis of

β -pinene, the key intermediate, *cis*-nor-bergamotinic acid was synthesized starting from methyl heptenone. In order to standardize the synthetic approaches involved in the ultimate synthesis of β -bergamotene from the above intermediate, some model experiments in pinene series have been undertaken.

Starting from ketocarboxylic ester (I) the cyclization was effected using sodium ethoxide to the β -diketone (II). Attempts to convert the diketo compound to nopinone (III) are in progress. Alternative routes for the synthesis of β -bergamotene starting from nopinone obtained from β -pinene are under study. Nopinone (III) was converted to tertiary alcohol (IV) by condensation with methyl lithium and this on treatment with HgO and Br₂, followed by exposure to UV light gave an oxide (V). Oxidation of (V) with chromic acid yielded a lactone (VI) which on reduction with LAH gave the diol (VII). The mono-tosyl derivative of (VII) will be converted to β -bergamotene. (VIII).



10.14 Naturally occurring anthraquinone pigments

A series of naturally occurring anthraquinone pigments are being isolated, characterized and synthesized.

Two other pigments, now designated as cassiamin B and C with reference to cassiamin A, a pigment whose structure has already been demonstrated, have now been isolated. Like cassiamin A, cassiamin B and C are derivatives of 2,2'-anthraquinonyl, two molecules of emodin and two molecules of chrysofenol respectively being linked together.

In connection with the structures of natural anthraquinone pigments, the NMR spectra and mass spectra of a series of anthraquinones containing methoxyl and other substituents are being examined. Synthesis of nalgiovensin is in progress.

The synthesis of kermesic acid has been undertaken. A substance with the authentic structure assigned to kermesic acid has been obtained, but it has not yet been possible to prove its identity with natural kermesic acid.

10.15 *Flavonoids and other plant pigments*

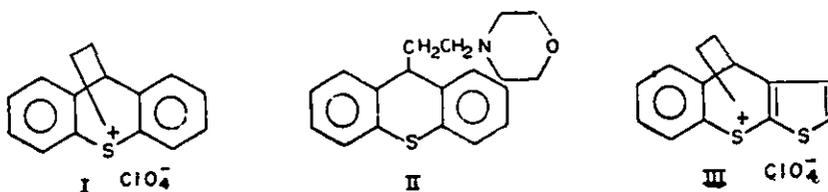
Attempts are being made to synthesize several naturally occurring flavones. Work on the structure of munetone, the infrared spectra of flavones and isoflavones, and the synthesis of a few flavones derived from iretol has been completed.

RP.11 SYNTHETIC ORGANIC CHEMISTRY

11.1 *Biologically active compounds*

11.1.1 *Thiaxanthylum salts*: The synthesis of 9,10-ethanothiaxanthylum perchlorate (I) mentioned in the last report has been completed. The compound was prepared with a view to study the biological activity. The synthesis was achieved according to the programme mentioned in the last report by the treatment of the thiaxanthene -9- ethanol with 70% perchloric acid and its structure was confirmed by elementary analysis, UV, IR and NMR data. The 9,10-ethane bridge could readily be broken at the hetero atom by the action of bases like morpholine to yield 1-N-morpholino-2-(9-thiaxanthyl) ethane (II) which provided additional proof of the structure.

Various other routes to the compound were tried starting with thiaxanthidrol but without success. The synthesis of thiophene analogue (III) is also under study.



11.1.2 *Synthesis of antifertility drugs* : The syntheses of the series of heterocyclic systems with a 11-thiasteroidal framework were undertaken to study their usefulness as antifertility and anti-cancer agents. Several key intermediates for their total synthesis were prepared from available starting materials and some of the experiments towards a total synthesis of the steroidal skeleton were successful.

11.1.3 *Carcinostatic compounds* : The sulphur analogues of 3,4-benzophenanthrene in which the sulphur atom occupies 1 or 2 position in the phenanthrene nucleus (I & II) are of interest in the study of carcinostatic activity.

As the proposed synthesis involves a dehydrogenation step it was thought profitable to study this step on a simpler and easily accessible model (III). The synthesis of (III) was effected starting from cyclohexanone and the dehydrogenation is being pursued.

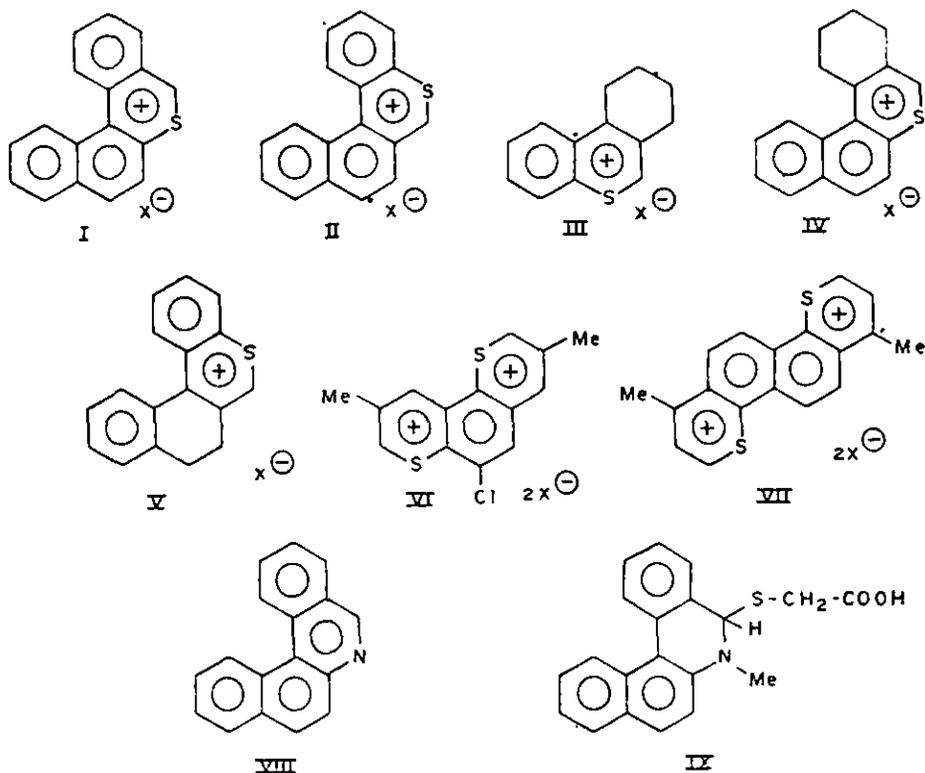
The synthesis of hydrogenated systems (I) and (II) were also carried out simultaneously and the perchlorate (IV) and (V) were synthesized starting from β -thio-naphthol and tetralone respectively.

In connection with the preparation of the above mentioned perchlorates it was found that the treatment of hydroxymethylene ketone with ethyl orthoformate in ethanol and acid did not give reported ethoxymethylene ketones in pure form: instead, NMR evidence indicates the product to be mixtures of ketones and acetals.

The synthesis of (VI) and (VII) which would be isolated as diperchlorates is also under study and spectral evidence have shown their formation and their actual isolation in quantity for testing purposes is in progress.

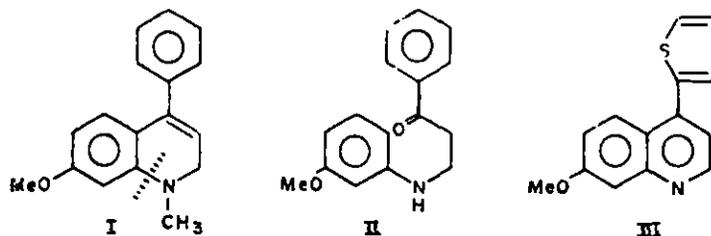
The synthesis of 10-N-methyl-9, 10-dihydro-3,4-benzophenanthridine-9-mercaptoacetic acid (IX) which would be of interest as a carcinostatic compound, and mentioned in the last report, is nearing completion.

The tetrahydrophenanthridine was dehydrogenated with selenium to phenanthridine (VIII). The methiodide from (VIII) has been prepared. The introduction of the mercaptoacetic acid group at the 9th position as in (IX) in order to make the product water soluble for biological testing purposes is in progress.



11.1.4 *Potent analgesics* : The synthesis of potential analgesics of the dithienyl butenyl amine type was started. 1-N-Methyl-1,2-dihydro-4-phenyl-7-methoxy quinoline (I) can be considered a benzene analogue of the above type if a hypothetical cleavage as indicated by the dotted lines in (I) is considered. The condensation of *m*-anisidine with the mannich base of acetophenone gave the ketone (II), which was cyclized with polyphosphoric acid in presence of trityl chloride to yield 4-phenyl-7-methoxy quinoline. The conversion to the methiodide and reduction to the dihydro derivative with sodium borohydride was carried out in good overall yields.

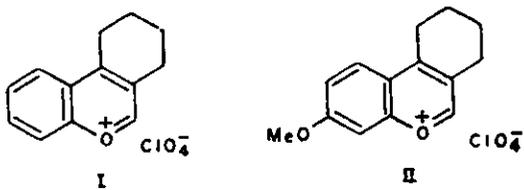
The replacement of acetophenone mannich base with 2-acetylthiophene mannich base gave the mono-thienyl analogue (III) and the replacement of *m*-anisidine by aniline yielded the phenyl derivative.



11.2 Studies in hydride transfer

11.2.1 *Thiachromanes* : The studies on the stereochemistry of hydride transfer at the ring junction during formation of thiachromanes were continued. The pure *cis*-thiachroman prepared by catalytic hydrogenation yielded a sulphone on oxidation which melted sharp at 152° ; while the thiachroman obtained by disproportionation and converted to the sulphone melted over a range 127-141°. This indicated a mixture, and VPC analysis showed a 77% *cis* and 23% *trans* ratio of products. Further confirmation of this was obtained through NMR studies of thiachroman and VPC analysis of Raney Nickel desulphurized products from both the samples.

Related studies are in progress with the oxygen analogues to study the nature and extent of participation by sulphur in the stereoselective hydride transfer. It should be pointed out here that 3,4- dimethylchroman obtained by disproportionation showed a *cis/trans* ratio of 50/50. The synthesis of perchlorate (I) has been completed and the structure confirmed by NMR analysis and the 7-methoxy derivative (II) is under preparation starting from *m*-methoxyphenol.

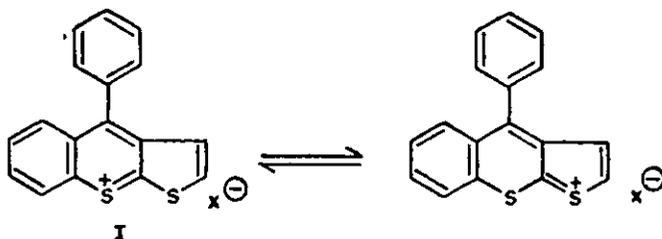


11.2.2 *Mechanism of formation of oxazine dyes and dioxazine pigments* : It was reported earlier that the mechanism of formation of oxazine dye (e. g. Meldola's blue) may involve an ultimate hydride transfer step. Methylene blue, a thiazine derivative, is observed to be formed by the action of trityl chloride on the dihydro derivative of methylene blue and the resultant triphenylmethene, as one of the products isolated, strongly indicated a hydride transfer process. In the case of triphenyl methane dyes also the leuco base yielded the dye with trityl chloride acting as hydride abstractor. The E.S.R. studies have ruled out the possibility of a radical mechanism as one of the alternative routes to their formation.

In connection with studies on hydride transfer during the formation of dioxazine pigments, attempts at obtaining direct evidence of its formation *via* the hydride transfer mechanism have been unsuccessful.

11.2.3 *Thianaphthelinium salts* : The synthesis of 4-phenyl-2,3-thieno-thianaphthalenium perchlorate (I) was mentioned in the earlier report, in connection with the study of delocalization of charge from one sulphur atom

to another within the ring system. The unstable 2,3-thienothianaphthalenium perchlorate has now been isolated and characterized. A detailed study of the NMR data on these compounds indicates that the charge delocalization does take place although this is not apparent from a study of their electronic spectra due to other effects.



11.3 Synthetic dyes

11.3.1 *Azoic dyes* : NMR spectral methods were applied to the study of azophenol-quinone hydrazone tautomerism. This is of general interest in connection with structures of azo and azoic dyes. The structures of three new azoic coupling components have been determined. The point of attachment of reactive dyes to the cellulose macromolecule are being investigated with the aid of NMR spectra; model derivatives of glucose are being prepared in this connection.

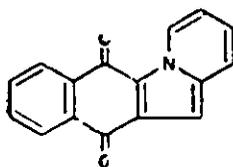
Orientation problems concerning benzanthrone and violanthrone derivatives are under study, mainly using NMR spectra. For the separation and purification of anthraquinonoid vat dyes it is convenient to convert them to the products of reductive methylation or acetylation. Solubility in organic solvents is thus greatly increased, and the products also become amenable to mass spectroscopy.

11.3.2 *Cyanine dyes* : The synthesis of mono-methine cyanine dyes is being continued. The condensation of 4-methyl-2-phenyl-thianaphthelinium perchlorate with 2-phenyl-thianaphthelinium salt gave a symmetrical monomethine dye whose structure was confirmed by elementary analysis and spectral data. Several samples of these dyes are being tested by a commercial firm for evaluating their photo-sensitizing action.

The action of various nucleophilic reagents on the thianaphthelinium cationoid system was investigated. The attack by hydroxyl ion on 4-phenyl, 4-thienyl, and 4-paramethoxy-phenyl thianaphthelinium perchlorates gave an almost equimolar mixture of thiachromin and thiachromene derivatives

whose structures have been established. The action of reagents like hydrazine hydrate and absolute methanol on 4-phenyl-thianaphthelium perchlorate gave highly coloured derivatives whose structures are under investigation.

11.3.3. *New heterocyclic vat dyes* : The pyrocoline ring system (I) which could be readily synthesized from 2,3-dichloro-1,4-naphthoquinone, ethylacetoacetate and pyridine is a potential intermediate for the synthesis of novel vat dyes. The preliminary attempts at converting the quinone (I) into an anthrone derivative by various routes were abortive and more work in this direction will be carried out. The complete reduction of the quinone to the naphthopyridazine will be attempted.



I

11.3.4 *Tris-arylsulphonium compounds* : The replacement of the triphenylmethane carbon atom with sulphur would lead to new types of basic dyes and the work was undertaken with a view to synthesize sulphur analogues of Malachite Green and Crystal Violet in the first instance. A study of their economics of manufacture and dyeing and fastness properties will be carried out.

11.4 *Conformational studies of Westphalen's diacetate*

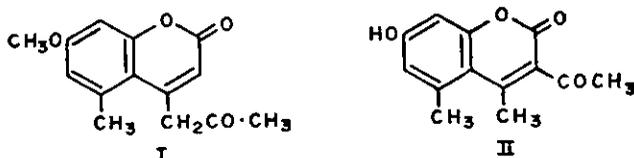
Ring B being trans-fused to ring C on one side, and fused to ring A on the other side, is very rigid in the usual steroids and is generally taken as an example of the rigid chair form of the cyclohexane ring. However, environments are studied wherein the conformation of ring B can become mobile and the ring can exist in alternate half chair conformations.

Thus, in Westphalens diacetate it is found that when a C_6 -substituent is β -oriented, the ring systems are A/B *quasi trans*, B/C *quasi cis* and when the C_6 -substituent is α -oriented, the ring systems are A/B *quasi cis*, B/C *quasi trans*. This is thus a very rare instance in the steroids wherein the B ring flips from one half chair conformation to another, by a change of configuration of the C_6 -substituent. ORD and C.D. measurements of the C_6 -ketone and further reactions with it show that it exists as a mixture of both the conformations mentioned above. The centrally located B ring thus shows an unusual conformational mobility in this type of steroids. (Paper 67)

11.5 4-Acetomethylcoumarins

The study is initiated to confirm the structures assigned to the Kostanecki-Robinson acylation products of β -orcacetophenone and its derivatives. An unambiguous synthesis of 4-acetomethyl-5-methyl-7-methoxycoumarin (I) was carried out and the product was found to be different from the Kostanecki-Robinson acylation product of β -orcacetophenone monomethyl ether to which the same structure (I) was assigned by the earlier workers.

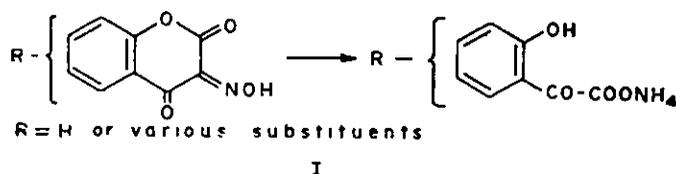
3-Acetyl-4,5-dimethyl-7-hydroxycoumarin (II) was synthesized by a new route as a possible alternative structure for the Kostanecki-Robinson acylation product of β -orcacetophenone but was found to be different from it.



11.6 Meerwin arylation of 4-hydroxycoumarins

3-Aryl-4-hydroxycoumarins are potential anticoagulants and oestrogens. Meerwin arylation reaction has been employed for their syntheses.

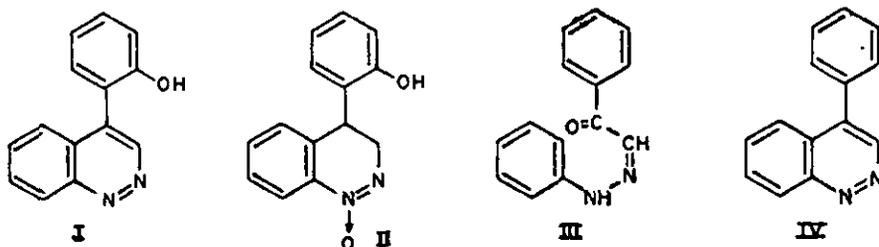
During the course of Meerwin arylation of 4-hydroxycoumarins a new group of compounds was obtained as by-product. Contrary to our earlier report, these compounds have now been established to be the hitherto unknown ammonium salts of *o*-hydroxyphenylglyoxalic acids (II) and this has been confirmed by synthesis. They are formed from another by-product of this reaction, namely, 2,3,4-triketochroman-3-oximes (I) possibly through an exceptional self-catalysed Beckmann type of transformation followed by hydrolysis and rearrangement of the resulting amide.



11.7 Synthetic studies on 4-arylcinnolines

Synthesis of hitherto unknown 4-(*o*-hydroxyphenyl)-cinnolines (I) and their N-oxides (II) was reported last year.

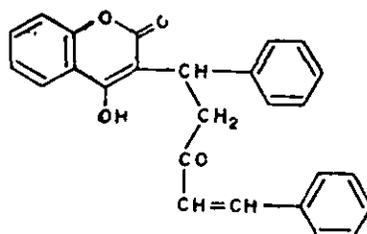
This new process has now been extended to a general method for the synthesis of 4-arylcinnolines (IV) from the *cis*-isomers of phenylglyoxal-2-phenylhydrozones (III).



11.8 New analogues of warfarin

In view of the anticoagulant and rodenticidal properties of warfarin, attempts are being made to synthesize some of its new analogues.

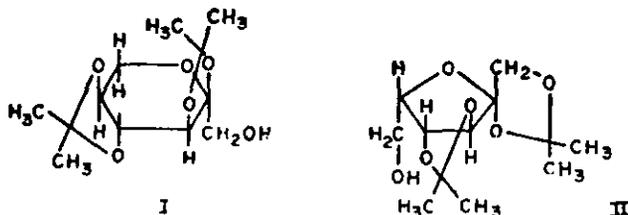
Condensation of warfarin with benzaldehyde gave an unstable product which has been isolated in pure state and assigned the structure (I)



11.9 Cyclic acetals and ketals of monosaccharides

This problem was taken up in connection with attempts to improve the yields of 2,3:4,6-di-*o*-isopropylidene- α -L-sorbofuranose, which is a key intermediate for the synthesis of vitamin C. New TLC techniques were developed and using these techniques many hitherto unknown cyclic acetals and ketals of various sugars were isolated and characterized.

On the basis of mass spectral studies, the structure of one of the new di-*o*-isopropylidene derivatives of L-sorbose which was earlier assigned the structure of 2,3:4,5-di-*o*-isopropylidene- α -L-sorbopyranose (I) was revised to 1,2:3,4-di-*o*-isopropylidene- β -L-sorbofuranose (II).



11.10 Transformation products of tricycloekasantalic and bicycloekasantalic acid

With an ultimate aim of synthesizing santalols which are the main perfumery components of sandalwood oil, different routes are being attempted.

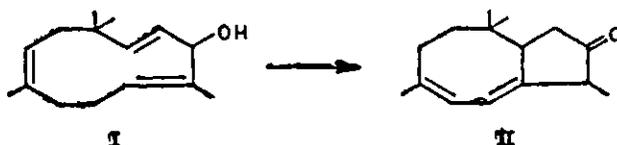
Starting from camphor, tricycloekasantalic acid was synthesized and was converted into pure α -santalene, α -santalic acid and α -santalol.

Bicycloekasantalic acid is an oxidation product of santalols. The crystalline "bicycloekasantalic" acid of Semmlar obtained by alkaline dehydrohalogenation of hydrochlorobicyclomethylekasantalate is shown to be a mixture of true bicycloekasantalic acid and isobicycloekasantalic acid. The structure of isobicycloekasantalic acid has been established by chemical degradation and synthesis. All attempts to purify "bicycloekasantalic" acid were unsuccessful. Wittig reaction of "bicycloekasantalal" with carbethoxymethyl triphenyl phosphorane gave a mixture of ethyl β -santalate and ethyl iso- β santalate. From this mixture ethyl- β -santalate was obtained in 85% purity and was subsequently converted into β -ekasantalic acid, methyl- β -santalate and β -santalol.

11.11 Base catalysed reaction of lithioethylene diamine

The reagent is very useful for isomerization and dehydrogenation of terpenoids. It is useful in synthesis of compounds which cannot be synthesized by conventional routes. The study of this reaction was extended to compounds like steroids and medium-sized ring compounds.

Humulene on treatment with this reagent furnished a mixture of two someric hydrocarbons presumably with the formation of bicyclic products. Characterization of these products is in progress. Zerumbone polymerized during the base catalysed reaction. Zerumbol (I) gave the bicyclic ketone (II) [2-keto-3,6,9,9-tetramethyl- Δ 5:6, 4:11-bicyclo(6:3:0)undecane] which has been characterized. The isomerized product of stigmaterol was oxidized by Oppenauer method to get the mixture of isomeric α , β -unsaturated ketones which on selective ozonolysis furnished a mixture of essentially two ketones. These were identified as androstenedione and progesterone. Androstenedione was separated in a pure form and identified. Progesterone could not be obtained in completely pure form.



11.12 *Perfumery chemicals from longifolene and camphene* (condensation with phenol)

This work has been undertaken with a view to develop new types of aromatic compounds.

The structure of the novel lactone, isolongifolanolide, prepared by the lead tetracetate oxidation of isolongifolol, was confirmed by converting it by a series of reactions to isolongifolane diol, keto-isolongifolic acid, keto-isolongifolol, isolongifolanol and isolongifolanone. Finally the ketone, isolongifolanone, was converted into the known hydrocarbon, isolongifolane, and compared with the standard sample. The condensation of longifolene with phenol in the presence of catalytic quantity of boron trifluoride etherate at 0° afforded a mixture of two ethers. The structures of these as well as that of the isobornylphenyl ether, obtained by a similar reaction of camphene with phenol, have been proved by spectral data and their stereospecific cleavage to the known alcohols with Li-liquid ammonia reduction. The separation of this alcohol mixture was achieved by converting it into a ketone mixture and separating one of them *via* semicarbazone formation. The condensation at an elevated temperature (100°) led to the formation of a complex mixture of *o*- and *p*-terpenyl phenols. The characterization was done by the spectral evidences.

11.13 *Synthesis of compounds related to selinane and elemene*

Junenol, saussurea lactone and 1-oxo-eudesmanes are known to occur in various plants. While studying the chemistry and the structures of these and their related compounds, new methods of their syntheses have been developed. All these compounds contain selinanic carbon skeleton. Santonin is one of the known pharmaceutically active compounds having the selinanic carbon skeleton. A systematic study of the synthesis and reactions of these related compounds has been undertaken with an ultimate aim of developing a commercial synthesis of santonin.

Tauremisin, a constituent of *Artemisia tourica willd* and *Artemisia vulgaris L.* and saussurea lactone have been synthesized. (Paper 100)

On the basis of this synthesis, a convenient route for the preparation of 2,3-*seco* steroidal 1,3-dienes has been developed. 3-Ketocholestane has been transformed to 2,3-*seco*-cholesta 1,3-diene. β -Elemene and elemol have also been synthesized.

11.14 *Santalene-longifolene series*

This work has been undertaken with an ultimate aim of exploring the possibility of synthesizing *iso*- β -santalene and *iso*- β -santalol from readily available natural products. It is expected that these products in santalene series will have perfumery properties.

It was thought that the acidic constituents of the sandalwood oil, such as teresantalic acid and tricycloekasantalic acid, will be useful intermediates in the proposed synthesis of *iso*- β -santalol. While isolating the above known constituents of the sandalwood oil, a new compound was isolated in pure form, which was further shown to be a keto-acid and named as ketosantalic acid (I). The structure elucidation and characterization of the compound was completed. During the attempts to synthesize (I) from *n*-bromotricyclene, contrary to the expectation, another compound (II) has been obtained. This has been characterized as a derivative of terasantalol.



11.15 *Transformation products in carvone and limonene series*

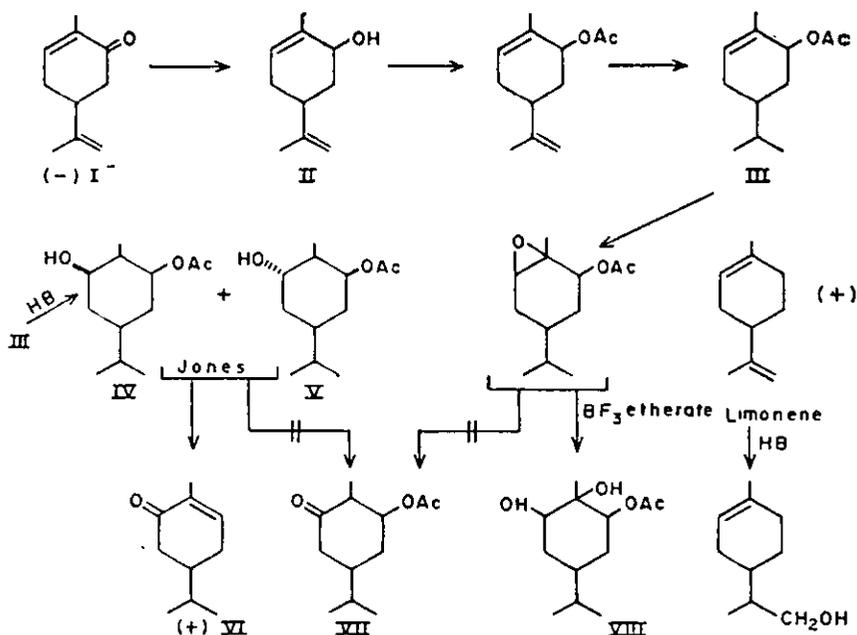
Our interest in these studies centres around the ultimate aim of synthesizing monocyclic and bicyclic naturally occurring compounds such as canarone, zinziberene etc.

Starting from (—) carvone (I), carveol (II) was obtained by LAH reduction, which was further converted to carvetoneacetol acetate (III), through the hydrogenation of the carveolacetate. On hydroboration of (III), epimeric mixtures of alcohols (IV) and (V) were obtained. With chromic acid oxidation, either of the alcohols or their mixture yields (+) carvetoneacetone (VI), and not the ketoacetate (VII). This can be mentioned as a useful method of changing the configuration in these series.

Another route through epoxide of (III) to obtain the ketoacetate (VII), was tried. The BF_3 -etherate treatment on the epoxide gave the diol acetate (VIII) and not the ketoacetate (VII).

Selective hydroboration was tried on limonene to obtain *p*-menthane-6-ene-9-ol, which has a new asymmetric centre at C_8 . The stereochemistry

at this centre is being studied and attempts are being made to convert it into a compound of known configuration and optical purity.



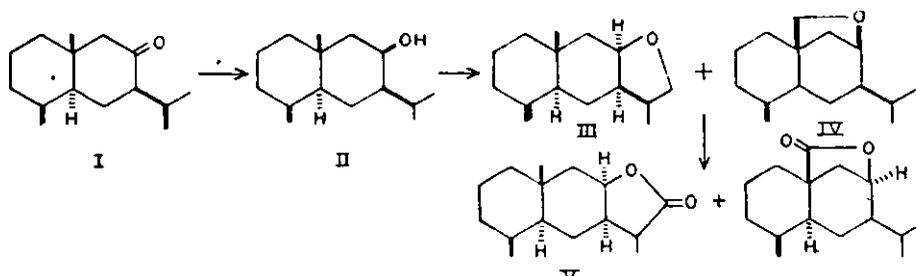
11.16 Transformation products of eudesmol

Eudesmol is a known naturally occurring compound of which the stereochemistry has been well established. In order to study the stereochemistry of some of the natural compounds isolated in this laboratory, attempts are being made to synthesize them or their derivatives from eudesmol.

The conversion of dihydroeudesmol into eudesman-6-one and eudesman-8-one was mentioned in the earlier report.

Eudesman-8-one (I) was reduced with LAH and the β -alcohol so formed (II) was oxidized by lead tetracetate to a mixture of two oxides (III & IV) which, on further oxidation with chromic acid, gave a mixture of two actones. One of these lactones has been identified as tetrahydroalantolactone (V). The other lactone has been shown to be the lactone of 8- β -hydroxy-eudesman-15-oic acid.

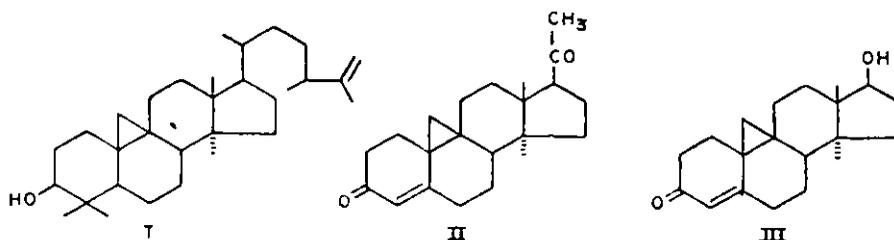
A similar series of reactions starting from the epimeric alcohol of (II) are being studied and a synthesis of an isomeric tetrahydroalantolactone with *trans* fused lactone system is in view. Eudesman-6-one was converted to dihydrojunenone by equilibration.



11.17 Utilization of opium marc

Opium marc, the waste material left after the extraction of morphine and other alkaloids from crude opium, contains a triterpene alcohol, cyclolaudenol, which can be obtained easily by solvent extraction. Cyclolaudenol (I) is characterized by the presence of a cyclopropane ring. As the tetracyclic triterpenes have been found to be very useful starting materials for the preparation of steroidal hormones of the type progesterone and testosterone, work has been undertaken on the transformation of cyclolaudenol (I) to steroidal hormone analogues (II) and (III).

Work on the degradation of the side chain by a new short route, through isomerization, allylic bromination and dehydrobromination, is in progress.



RP.12 PHYSICAL ORGANIC CHEMISTRY

12.1 Applications of NMR spectroscopy

NMR spectroscopy has been used in the solution of analytical problems and in the identification of imported materials known only by their trade names. In view of the usefulness of this technique, considerable attention has been devoted to basic studies leading to new applications, and some very significant results have been obtained. For example, earlier work demonstrated for the first time the use of long range spin-spin coupling measurements in the study of bond orders in aromatic compounds. The value of this technique has now

been recognized by other workers. The question of the Mills-Nixon Effect, which has been debated for more than three decades, has been finally answered with the help of such measurements in our laboratory. We have now obtained, by a new technique, valuable evidence relating to another controversial issue, namely, the concept of hyperconjugation.

12.1.1 *Aromatic compounds* : In continuation of the earlier work on the use of long range spin-spin coupling for sensing π -electron distribution in aromatic compounds, it has been shown that the methyl bandwidths of the isomeric toluic esters and nitrotoluenes are indicative of the bond length changes that accompany substitution of the benzene ring by the nitro and carboxyl groups.

The controversial concept of hyperconjugation has been re-examined using a novel technique. Methyl *o*-nitrobenzoate and its derivatives, which form a sterically hindered system, have been used to study the interaction of the acceptor groups of these molecules with alkyl and other donor groups across the aromatic ring. The interaction results in conformational changes for the acceptor groups involved and it is reflected in the PMR chemical shifts of the corresponding *ortho* protons. With methyl as the donor group the effect is stronger than with the *t*-butyl group, indicating that hyperconjugation of even the 'sacrificial' type is important and that its effects are measurable in the ground states of molecules.

The NMR spectrum of 5,10,16,17-tetramethoxyviolanthrene (the reductive methylation product of 16,17-dimethoxyviolanthrone) has been analysed and the assignments for all the main groups of protons given on the basis of the symmetry of the molecule and ring current effects that may be expected. This analysis has laid the basis for providing the chemical shift assignments for similar derivatives. Thus, from the NMR spectrum of the reductive methylation product of the dibromo derivative of 16,17-dimethoxyviolanthrone it was concluded that the bromine atoms are at the 3 and 12 positions.

12.1.2 *Structural and stereochemical applications* : The stereochemistry of cyanomaclurin has been reconsidered in the light of additional NMR data and it has been shown that inversion of the configuration suggested earlier for the 3-position is necessary. Synthetic work has been found to support the basis for this conclusion.

The application of NMR spectroscopy in the study of the azo-phenol-quinone hydrazone tautomerism has been examined using a number of compounds. The deshielding effects of the azo group on the *ortho* and *peri* protons have been used for the identification of the two forms. The lack of aromatic

character in one of the aromatic rings in the hydrazone form of such systems and the associated diamagnetic shifts have also been found to be of assistance in making spectral assignments. The data obtained have further amplified our knowledge of these tautomeric systems. It has been possible (for the first time) to determine the equilibrium constant for one pair fairly accurately.

12.2 *Studies on the Mills-Nixon effect*

A recent NMR spectroscopic study has shown that the mobile bond order of the C₄-C₅ bond of indane is larger than that of the C₅-C₆ bond indicating localization of π -bonds in a sense opposite to that suggested by Mills and Nixon.

The reactivity of the ethylene thioketals of 5- and 6-bromoindan-1-ones towards lithium diethylamide has been examined. The latter compound does not react with the reagent while the former gives a complex product mixture that has not yet been analysed. The lack of reactivity of the 6-bromo derivative gives some measure of support to the earlier conclusion regarding bond fixation in this system.

12.3 *Carbonium ions*

In connection with the measurement of barriers to rotation in carbonium ions that can be generated from aromatic aldehydes, an exploratory study has been undertaken on the preparation of stable carbonium salts from *p*-substituted benzaldehydes. These have so far been regarded as being too unstable to be isolated.

A method has been worked out for the preparation of a series of *p*-substituted α -acetoxybenzyl perchlorates by the action of acetic anhydride and perchloric acid on benzaldehydes. The compounds can be obtained pure either as crystalline solids or as viscid masses that do not crystallize readily. The stability of these salts varies with the nature of the *p*-substituent. Some of them are stable over a period of several days. All of them are highly sensitive to moisture, in contact with which decomposition to the aldehydes proceeds with extreme ease.

12.4 *Electronic spectra*

The electronic absorption spectrum of 16,17-dimethoxyviolanthrone, one of the most important of vat dyes, was discussed in terms of steric hindrance in some early studies. A recent study of 16, 17-disubstituted violanthrones from this laboratory has shown that this interpretation is incorrect and that

the long wave length (bathochromic) shift accompanying methoxyl substitution in the 16 and 17 positions may be traced to electronic repulsion in the ground state and 'internal solvation' in the excited state. It was shown that, on theoretical grounds, only hypsochromic shifts could be expected from steric effects of substituents at the positions concerned. This has also been verified experimentally.

The spectra of the 16-amino and 16,17-diamino derivatives have now been obtained and the data seem to accord well with the conclusion reached earlier.

12.5 *Stereochemical studies by PMR spectroscopy*

12.5.1 *Stereochemistry of axial and equatorial acids* : Using diterpene acids as model compounds and utilizing solvent effect on spectral signals, methods have been evolved to find (a) whether a carbon bearing a carboxyl group also holds a methyl group on it, (b) if so, what the conformation of this methyl group is, and (c) the type of fusion of the ring holding the carboxyl group with the adjacent ring. This has been directly applied to find the stereochemistry of two diterpenes, salvin and picrosalvin.

12.5.2 *A method to find the stereochemistry of the side chain γ -lactone* : Model compounds containing rigid cyclohexane rings to which γ -lactones are fused, both *cis* and *trans*, in the angular as well as linear positions have been prepared. The PMR spectra of these compounds were determined in aromatic and non-aromatic solvents. From these data a new method has been evolved to find the stereochemistry of the side chain of γ -lactones for which no simple method existed before. The method depends upon the conception of the side chain as *quasi axial* and *quasi equatorial* and noting the considerably different solvent shifts of its protons in these two conformations.

12.6 *Mass spectrometry*

Work on commissioning a double focussing mass spectrometer CEC-21-110 B for characterization and estimation of organic compounds of fundamental and applied significance, has been completed.

12.6.1 *Applications of mass spectrometry—Developmental work*

(a) *Structure determination* : A few samples of terpenes, oxygen and sulphur heterocycles, anthraquinone derivatives and polycyclic compounds have been analysed to explore the possibilities of using this tool as a physical probe in elucidating the structure of unknown compounds of the same type.

(b) *Stereochemical studies* : Very little is known about the relationship between stereochemistry and fragmentation modes. In the case of certain bridged systems of known stereochemistry, the fragmentation modes have been established. This correlation will be useful in establishing the stereochemistry of unknown compounds.

(c) *Biogenetic studies* : Biogenetic studies are normally carried out with the help of radio-tracers. Using stable isotopes and employing spectral methods, work on the biogenesis of aflotoxin has been undertaken. Aflotoxin is a carcinogenic compound produced by a mould which grows in groundnut.

(d) *Electron impact studies* : Behaviour of various simple organic compounds under electron impact has been studied to get additional information on skeletal rearrangements.

RP.13 MICROBIOLOGY

13.1 *National Collection of Industrial Microorganisms*

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

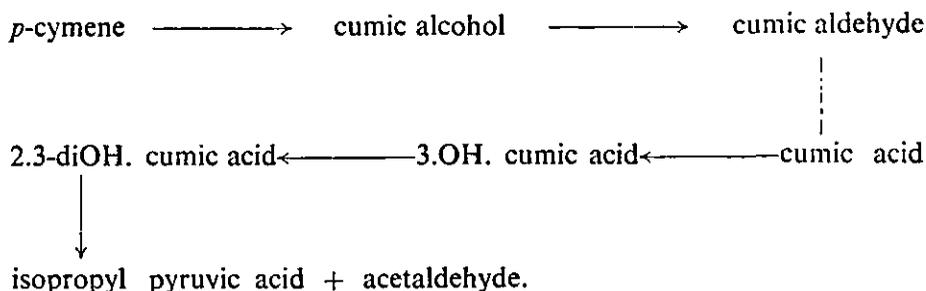
The routine maintenance and subculturing of the cultures and the testing of cultures for their biochemical performance were continued. 90 new cultures were added to the collection, 569 cultures were despatched to various industries and institutions. Several agar samples received from CSMCRI, Bhavnagar were tested for their suitability for growth of microorganisms.

13.2 *Microbiological transformation of terpenes*

Microorganisms have been known for a long time to bring about useful chemical conversions which are difficult to achieve with chemical agents. With this view the present work is undertaken to convert easily available terpenoid hydrocarbons into oxygenated products of potential interest to the perfumery industry as well as to elucidate the biochemical mechanism underlying these transformations.

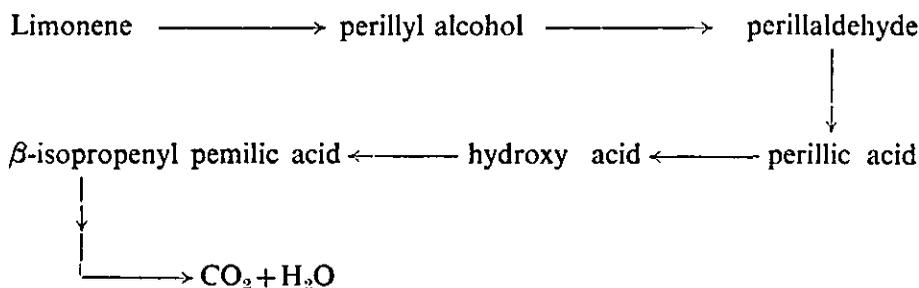
13.2.1 Bacterial transformations

(a) Fermentation of *p*-cymene : Degradation of *p*-cymene by the pseudomonad, PL-strain, has been studied and the following biodegradative pathway has been formulated based on isolation and oxidation of a number of compounds which could be regarded as intermediates.



Growth as well as adaptive enzyme studies have further substantiated the above plausible pathway. Work on the studies of various enzymatic systems involved in these transformations is in progress.

(b) Fermentation of limonene : A soil pseudomonad, PL-strain, capable of growth on limonene, has been isolated by enrichment culture technique. Among the fermentation products carveol, carveone, dihydrocarvone, 8-*p*-menthene-1, 2-*trans*-diol, 8-*p*-menthene-1-ol-2-one, perillic acid, β -isopropenyl pemilic acid and 4,9-dihydroxyphellandric acid have been isolated. Syntheses of dihydrocarvone, 8-*p*-menthene-1, 2-*trans* diol, 8-*p*-menthene-1-ol-2-one, have been completed in order to confirm the structure and the stereochemistry of the fermentation products. The following pathway for the degradation of limonene has been arrived at, based on growth and adaptive enzyme studies.



The enzymes for dehydrogenations of perillyl alcohol and aldehyde have been studied in this organism . Perillyl alcohol dehydrogenase has been purified to nearly 35-fold from the cell-free extract, and some of its properties have been studied. The following points were noted:

(1) The pH optimum for the reaction is 9.4; (2) The activity is inhibited by heavy metal mercurials and other SH-reagents. (3) Besides perillyl

alcohol, many other terpenic as well as aromatic alcohols serve as substrates. Based on this requirement certain structural features for the activity have been shown.

Perillyl aldehyde dehydrogenase has been purified about 10-fold and its properties have been studied. Cysteine was found to be necessary for maximal activity. Preincubation of the enzyme with cysteine and NAD was essential before addition of the substrate. Optimum pH for the enzyme is 10.0. Heavy metals and SH-reagents inactivated the enzyme, which showed a broad substrate specificity.

Fermentation studies with β -isopropenyl pemilic acid are in progress to elucidate the complete degradative pathway of limonene by this organism.

(c) *Fermentation of Δ^1 and Δ^3 p-menthenes* : Earlier studies have indicated that a *p*-menthenoid type intermediate is involved in the degradative pathway of α and β -pinenes by PL-strain; hence, fermentation studies on Δ^1 and Δ^3 *p*-menthenes were undertaken. A pathway for Δ^1 *p*-menthene involving phellandrol, phellandral, phellandric acid, 2-OH-*p*-menth-7-oic acid and β -isopropylpemilic acid has been postulated. Growth and adaptive enzyme studies with these intermediates have further substantiated the postulated pathway of degradation.

The organism grows on Δ^3 -*p*-menthene after a period of 48 hours, and from the fermentation medium several intermediates have been isolated. Amongst these, the presence of menthol has been tentatively shown. Work is in progress to identify these intermediates and to postulate a probable pathway for its degradation.

13.3 Transformation of *Kurchi* alkaloids

Holarrhena antidysentrica, commonly known as *Kurchi*, contains mainly the 18-substituted steroidal alkaloids which have attracted attention as the potential precursors of 18-oxygenated steroids, principally that of aldosterone. Earlier work involved the standardization of the methods of isolation of alkaloids and stepwise conversion of conessine, isoconessimine, conessimine and holarrhimine to 18-hydroxyprogesterone.

The present work involves the reinvestigation of the reaction, conessine— \rightarrow Schiff's base. The Schiff's base on treatment with 1 mole, of perbenzoic acid yielded the N-oxide which was cleaved with sodium metaperiodate to its oxime. Nitrous acid treatment of the oxime yielded 18-aldoprogesterone in good yield.

Identity of 18-aldoprogesterone was confirmed by synthesizing the same compound by two different methods.

Further studies on the microbiological incorporation of OH-groups, at C-11 and C-21 position to give the expected compound, aldosterone, are in progress.

13.4 *Metabolism of C₅- and unnatural C₄-dicarboxylic acids*

Studies on the mechanism of the hydration of citraconate and maleate and to purify the concerned enzymes have been continued.

Citraconate was found to be hydrated to laevorotatory citramalate by a new enzyme called citraconase. The purification of citraconase has been continued and a 25-fold purification has been achieved.

The enzyme malease has also been found to be present in the citraconate-cells. It has been purified 10-fold. It converts maleate into dextrorotatory (unnatural) malic acid. This is distinct from citraconase.

13.5 *Isolation of mutants for the estimation and production of useful amino acids*

Some other laboratories in India have been working on the production of proteins (yeasts) by growth of microorganisms on hydrocarbons. Efforts in this laboratory are directed towards the isolation of mutants or strains capable of synthesis and secretion of the nutritionally important amino acids.

Several mutants of *Serratia marcescens* which require amino acids for growth have been isolated and will be used for screening amino acid-producing mutants of other species.

RP.14 GROWTH OF PLANT CELLS

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

The requirements for the continuous growth *in vitro* of cells from different plants such as opium, cholai, digitalis etc., were determined. Twenty five

plant cell cultures are being maintained at present of which some were isolated and established for the first time in this laboratory. Viable maize callus and root culture was also established.

Studies on the nutrition of maize tissue isolated in this laboratory were continued and the effect of pH and temperature, amino acids, nucleotides, carbohydrates, auxins and kinins was tested. It was observed that this cereal culture, unlike most other callus cultures, grew very rapidly on starch.

Two new callus cultures (wheat and jowar) of cereal tissue were established and their viability on continued subculture and nutritional requirements are being studied. Work on two other cereal cultures (rice and bajri) is also in progress.

A comparison of the crown gall tumour and normal parthenocarpic tissue showed no significant difference in their ubiquinone content or in the nature of the isoprenologue of these tissues. Work on the isolation of normal and tumour cultures of tomato and sunflower is being continued.

Long range work on defining the conditions for obtaining single cell cultures from different tissues, which is in general difficult with plant tissues, is being continued.

RP.15 ENZYMES

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

15.1 *Hexokinase*

Animal tissue hexokinases have not hitherto been obtained in pure form. A new method for the solubilization of the particulate hexokinase of brain was discovered and the enzyme was purified till it was 85% pure as shown by ultracentrifugal studies.

Studies on the kinetics of the purified brain hexokinase were continued. Using pyruvic kinase and lactic dehydrogenase for the estimation of adenosine diphosphate formed in the hexokinase reaction and with mannose as substrate, 50 % inhibition was observed at 10^{-5} M glucose-6-phosphate. The inhibition was partly reversed by inorganic phosphate. Adenosine

diphosphate inhibition was non-competitive with respect to adenosine triphosphate. Studies on kinetics, optimum pH and the effect of different inhibitors and other compounds and metals were completed.

Methods were developed for the isolation in soluble, stable form of heart and rabbit muscle hexokinases, and both the enzymes were purified 5 to 10-fold. Further work on the isolation of the insoluble enzyme of heart is being continued.

15.2 *Phytase*

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

The enzyme was purified about 50-fold by fractionation with solvents and by the use of different adsorbents. It was observed that the hydrolysis of three phosphates of phytate was rapid and prolonged incubation with large amounts of enzyme was necessary to release one or more phosphate groups.

15.3 *DPNase*

The isonicotinic acid hydrazide-insensitive DPNases have been purified from animal tissues, but the isonicotinic acid hydrazide-sensitive enzyme from ox brain has not hitherto been obtained in soluble form. A new method was found for preparing the enzyme in soluble form from ox brain.

The partially purified soluble enzyme was found to be extremely stable over a wide pH range (2 to 12) but the enzyme rapidly reaggregated and became insoluble especially under acid conditions. Methods for the prevention of reaggregation of the enzyme and its purification are being studied.

15.4 *Acetylcholinesterase*

Acetylcholinesterase plays an important role in the metabolism of brain and nerve and has been obtained in soluble form and purified to a considerable extent from electric organs of some fish. A new method has been worked out for the preparation of soluble acetylcholinesterase from ox brain. Most of the work was carried out with caudate nucleus and the enzyme was purified about 40-fold by DEAE chromatography.

When the solubilized enzyme was purified about 40-fold it became unstable on further fractionation with different adsorbents. Suitable conditions for

stabilization of the enzyme were determined and the enzyme has been purified another 30-fold to obtain a specific activity of 25,000 units per milligram compared to the initial specific activity of 10 to 20. A rapid spectrophotometric method with phenylacetate as the substrate was standardized for routine activity determinations.

15.5 Citrate - oxaloacetate lyase

The enzyme citrase, which cleaves citrate to oxaloacetate and acetate is induced in cells of *Aerobacter aerogenes* grown on citrate. The enzyme has been obtained in pure form and has also been applied to a rapid and accurate spectrophotometric assay of citrate in biological materials.

Two aspects of the enzyme are being studied :

1. Active sites of citrase, and
2. Citrase induction.

1. Citrase forms an inactive complex with oxaloacetate. On the basis of sodium borohydride reduction, one of the active sites involved in the binding of the inhibitor appears to be an amino group on the enzyme molecule. Several organic acids structurally related to oxaloacetic and citric acids have also been found to form inactive complexes with the enzyme.

The subunit structure of the enzyme molecule is also being studied.

2. For studies on enzyme induction in *Aerobacter aerogenes*, conditions have been established for the preparation of spheroplasts of the organism.

15.6 Nitrate and nitrite reductases

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

The isolation of *A. fischeri* nitrite reductase in an ultracentrifugally homogeneous form has permitted the elucidation of certain of its physico-chemical properties. The enzyme was characterized as a c-type cytochrome and is auto-oxidizable.

The molecular weight of nitrite reductase from *A. fischeri* as determined by the Archibald's method was found to be of the order of 100,000. Nitrite reductase activity of the enzyme was inhibited by CO and cyanide but its reaction with oxygen was not inhibited by these reagents. The enzyme probably mediates the cyanide-resistant respiration in *A. fischeri*. Data obtained suggest

that the reduction of nitrite and hydroxylamine, but not of sulphite, is catalysed by the same enzyme in *A. fischeri*.

Preliminary data obtained indicated that nitrate reductase from *A. fischeri* consists of several subunits. The kinetics of the reformation of the enzyme and the regulatory mechanism of its formation are being studied. Attempts to develop a temperature-sensitive repression system for nitrate reductase induction in *A. fischeri* have met with no success.

A method for the estimation of hydroxylamine in the presence of reduced pyridine nucleotides, which are known to cause interference in the chemical test, has been developed.

RP.16 PHYSICO-CHEMICAL STUDIES OF POLYMERS

16.1 *Solution properties of polymers*

The ultimate properties of polymers depend upon their chain dimensions, usually represented by their molecular weights. Viscosity measurements of polymer solutions is the simplest method for the determination of molecular weights. Such calculations of molecular weights from viscosity measurements, however, involve the knowledge of two parameters (constants) which have been established on the basis of absolute methods of molecular weight determination such as light scattering, osmotic pressure measurements etc.

A new single parameter method of determination of molecular weight of polymers from their solution viscosities has been developed for polystyrene. It was later extended to systems such as poly-methylacrylate, poly-vinylacetate, poly-*p*-chlorostyrene and azeotropic copolymer of *p*-chlorostyrene and methylmethacrylate. These studies have now been extended to poly-methylmethacrylate.

The values of $[\eta]_R$ correlate well with the square root of the molecular weight but the constant of proportionality is more than twice the value obtained by Flory-Schaeffgen method. It has been inferred that the unperturbed dimensions of poly-methylmethacrylate are higher in solid or concentrated solutions in comparison with those obtained from studies of dilute solutions.

16.2 *Stereospecific polymerization*

Stereospecific polymers such as poly-propylene are well known for their superior properties. Although the technology of their production and application etc. is well advanced, the basic mechanism involved in this type of polymerization is not thoroughly established.

Studies on different monomer-catalyst systems have therefore been undertaken and some of the results reported earlier.

Polymerization of styrene with $VCl_4-Al(C_2H_5)_3$ and $VCl_4-Al(iBu)_3$ systems in presence of *n*-hexane was carried out. It was found that formation of catalytic species is complete at Al/V molar ratio of 3 in the case of $VCl_4-Al(iBu)_3$ system. Reaction was found to be of first order with respect to monomer concentration in both the systems, whereas with respect to catalyst system the order was one for VCl_4-AlEt_3 and zero for $VCl_4-Al(iBu)_3$ system. These catalyst systems gave much better stereospecificity than that obtained by the reaction of $VOCl_3$ with different aluminum alkyls presumably due to stronger bonding of monomer to vanadium in the catalyst complex. Activation energy and effect of zinc diethyl confirmed the coordinated anionic mechanism for the two systems.

A syndiotactic high molecular weight poly-methylmethacrylate (PMMA) was obtained when the the polymerization was carried out with $VOCl_3-Al(C_2H_5)_3$ system at 40° . This is the first time when a syndiotactic PMMA has been obtained with ionic catalyst at temperature above 0° .

In the previous studies reported for the polymerization of styrene with $ZrCl_4$ or $ZrCl_3$ in combination with different organometallic compounds, it was observed that these catalyst systems display dual role of first accelerating and later retarding the reaction. With a view to verify whether the phenomenon was a characteristic of zirconium complexes, or the monomer had some role to play in this typical behaviour, polymerization of isoprene was carried out with $ZrCl_3-Al(C_2H_5)_3$ catalyst system in toluene at 40° . At very high catalyst concentrations, the rate of polymerization decreased with isoprene as well, indicating that the behaviour is characteristic of zirconium complexes, but the concentration at which the fall begins depends on the monomer used. The rate of polymerization with isoprene was much lower as compared to that obtained with styrene.

16.3 *Physico-chemical studies of Indian silks*

Although extensive work has been carried out on the characterization and study of the composition of *Bombyx mori*, very little information is available on the physico-chemical properties of other common Indian silks such as Muga, Eri and Tussah.

Since structure and function of proteins are closely related at the molecular level, the work has been undertaken to determine the molecular parameters and relate them with the physical properties and mechanical behaviour.

In order to standardize the procedures of characterization, a method of separation of sericin from the *Bombay mori* fibre with the least possible damage to the silk fibroin, has been worked out. In the first instance work on characterization and solution behaviour of silk fibroin in known solvents (salt solution) has been undertaken.

Preliminary work on the molecular weight determination by light scattering in aqueous LiBr solution has been done at isoelectric point and some other useful pH values. It has been found that molecular weight depends on the LiBr salt concentration and its pH.

16.4 Degradation of long chain molecules by ultrasonics

The ultrasonic degradation has some resemblance to mechanical degradation i.e. mastication and the process is investigated on different industrially useful polymers. Studies are being made on degradation of butyl rubber.

The rate has been studied with samples (m.wt. in the range of 0.6×10^6 to 1.6×10^6) having initially the different degree of polymerization $(\overline{DP})_0$. It has been observed that both the rate parameters K and the final value $(\overline{DP})_\infty$ of the degree of polymerization are influenced by $(\overline{DP})_0$ values. Lowest $(\overline{DP})_\infty$ is obtained when the degrading molecules have the largest chain length at the beginning. The values of $(\overline{DP})_\infty$ are appreciably influenced by experimental conditions such as viscosity of solution, intensity of irradiation and $(\overline{DP})_0$ of the degrading samples. All these parameters have not been critically controlled by different investigators and hence considerable discrepancies in these values have been reported.

RP.17 GRAFTING ON CELLULOSE

Grafting of cotton with acrylonitrile was carried out with an ultimate aim of improving its anti-fungal and to some extent anti-crease characteristics.

By chemical methods, grafting upto 80% was observed. A 25-30% grafting was also obtained by γ - irradiations.

There was no loss in tensile strength with chemically grafted cellulose, whereas the radiation grafted samples showed considerable fall in tensile strength. The grafted samples were examined for their resistance to selected microbiological organisms (commonly found in Indian soil) and those having more than 30% grafting were found completely resistant to fungus growth.

RP.18 CHEMICAL ENGINEERING STUDIES

18.1 Reaction models and reactor design

Models have been developed for the oxidation of benzene and toluene and a rate equation has been determined for the hydrogenation of anacardol to tetrahydrocardol.

The kinetics of the ethylation of aniline has been fully studied and plausible models have been proposed for each of the independent reactions in this complex system. Criteria have been defined for the optimum combination of mixed and tubular reactors and charts have been prepared for the design of adiabatic reactors (with back mixing). Studies are also in progress on systems involving absorption and chemical reaction, and on the kinetics of the amination of alcohols. Experimental work has been commenced on pulsed fixed bed reactors and on models for diffusion in a catalyst pore.

18.2 *Studies in fluidization*

Fluidization is one of the very important operations in the chemical industry, but several aspects of fluidization still require theoretical and experimental examination.

A new and completely generalized method for the prediction of the onset of fluidization has been proposed.

The performance of a semi-fluidized reactor has been studied and a new reactor utilizing this principle has been proposed. The superiority of this reactor over the other types of reactor for exothermal reactions has been experimentally established. Further, a fluidized bed reactor from plastic sheets and tubes has been designed for examining the use of fluidization for heating industrial reactors. A theoretical analysis of the uniformity of fluidization has been made and an experimental assembly for testing the proposed equation has been set up.

18.3 *Studies in mass transfer*

Theoretical and experimental studies have been carried out to elucidate certain aspects of mass transfer.

Investigations have been carried out on the use of pulsed extraction columns for improving the efficiency of extraction by pulsation. Considerable computation has also been carried out for proposing a generalized equation for liquid-liquid extraction.

Experimental work on mass transfer during drop formation has been completed. A model for mass transfer during drop formation has been proposed, which involves circulation patterns inside the bubble analogous to magnetic force lines. The experimental data uphold the validity of this model.

The conventional rotary disc contactor (RDC) has been suitably modified to enhance mass transfer rates. This can be effected by improving

the mode of drop formation and decreasing back mixing. Under similar set of operating conditions, it has been possible to cut down HTU values in a modified RDC upto about 50% of the conventional RDC. This could also help lower power requirement. Mass transfer was studied with benzene-acetic acid-water and flooding with kerosene-water and benzene-water systems. The study is being concluded.

18.4 *Estimation of thermodynamic and transport properties*

Often it is not possible to experimentally determine some of the properties required in process design and hence these have to be estimated. Work on the development of improved estimation procedures for different transport and thermodynamic properties has been undertaken. These will also be determined experimentally.

An improved method has been developed for estimating the diffusion coefficient in liquids and also for estimating the latent heat of vaporization. The method for latent heat estimation is being further improved. A beginning has been made for setting up an apparatus for determining the more important properties.

18.5 *Interfacial tension in two and three component systems*

Interfacial tension in binary and ternary liquid-liquid systems is of considerable importance in connection with some chemical engineering problems. Various equations have been proposed. These have been tested mostly with data on aqueous systems.

Interfacial tension in some non-aqueous binary liquid systems have been determined using the drop volume method. Some known correlations are being tested with our experimental and spare literature data. Effect of temperature on interfacial tension of such binary system is also being investigated.

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APPENDICES

A-I SERVICE PROJECTS

1. *Physico-analytical work*

Analytical and testing work was conducted on the following samples : butyl phthalate; silica gel; calcium halophosphate; sodium diethyl dithiocarbamate; phenoxyacetic acid; sodium meta-periodate; 3,5-dinitrobenzoyl chloride; ZnO for trace impurities; silicon carbide for impurities; aluminium chloride; ferrites; phosphorus; phenacetin; chromium based ferric oxide catalysts; mineral similar to soapstone; monochloroacetic acid; silver foil for trace impurities; lac dye ash and stainless steel.

2. *Mass spectroscopy*

275 samples were analysed to solve problems connected with characterization, structure elucidation and stereochemistry of organic compounds.

3. *Microanalysis*

Microanalysis of organic compounds for various elements (C, H, N, halogen, sulphur), functional groups (methoxyl, acyl, C-methyl, N-methyl, active hydrogen), molecular weight, etc., was carried out.

2949 analyses for elements and 181 for functional groups were carried out. Modifications of the existing microanalytical methods for their wider applicability were studied. A rapid Micro-Dumas method is being standardized for the estimation of nitrogen in organic compounds.

4. *Spectroscopic work*

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

Number of samples studied :

NMR	..	1501
UV, visible & NIR	..	560
IR	..	4500

5. *VPC analysis*

6,226 samples were analysed.

6. *X-ray patterns*

170 X-ray powder patterns were obtained.

7. *Instrumentation*

Servicing and maintenance work of the following special equipment in NCL was routinely done.

NMR, Mass spectrometer, IR, UV and visible spectrophotometers, X-ray machine, pH meters, colourimeters, potentiometers, gas chromatographs, electron diffraction camera, electron microscope, ultrasonic generator, Sova recorders and nuclear instruments.

Running and maintenance of the liquid air plant and supply of liquid air to various groups in NCL were attended to.

Total number of jobs completed : 425.

8. *Workshop*

Special equipment fabricated :

	Item	Nos.
1.	Fume extractors (Exhaust blowers)for fume hoods.	.. 13
2.	Snowman (dry ice making unit)	.. 3
3.	Thin layer chromatography applicator funnel type.	.. 3
4.	Thin layer chromatography applicator (desaga type)	.. 5
5.	M.S. pressure reaction kettle (250 lbs./sq. inch) with steam jacket, stand and driving arrangement complete. Capacity-40 liters.	.. 1
6.	M.S. evaporating pans with fittings, size 4 ft. dia.	.. 4
7.	Electromagnet with inclined stand to hydraulically operated lifting arrangement	.. 1

Total number of jobs completed : 2818.

9. *Glass blowing*

Jobs completed : 5102.

5567 standard ground glass joints were fabricated.

10. *Technical services*

The following NCL processes were evaluated for their economic aspects: Styrene DVB-anion exchange resins; hard ferrites; phenoxyacetic acid; theophylline; VPC prototype unit.

Economic evaluation and cost estimates are in progress on the following projects : β -ionone; *l*-menthol; costus root oil; citronellal from citral; aminotriazole; double boiled linseed oil substitute; rutile titanium dioxide.

More than 500 enquiries from different parties were attended to. Non-technical notes on various NCL processes were supplied to about 100 parties.

Negotiations were conducted for the release of different NCL processes and for undertaking new sponsored projects.

The annual report of NCL for 1965-66 was compiled, printed and circulated to about 500 institutions and industries. The half-yearly report for April to September 1966 and the research programme for 1967-68 were compiled. A report on various projects in NCL giving the background, actual work, and market potential was compiled for the Estimates Committee. A summary of the present position of NCL processes released was compiled.

For the participation in four exhibitions, several pictorial charts were prepared. Participated in Expo 67 exhibition, Canada, by sending a model for electron diffraction camera, a few samples and write-ups.

Market survey and price fixation for 316 chemicals included in FCP catalogue were carried out.

Work on the computation of average overhead expenditure per scientist at the NCL was carried out.

Routine work on compiling research utilization data, CSIR news, attending to visitors, technical consultations and advice, collection of commercial information, project follow-up work, rendering photographic and draughtsman services, was carried out.

A-II SERVICES RENDERED TO OUTSIDE PARTIES

1. *Supply of cultures*

569 cultures from NCIM were supplied free of charge to various parties.

2. *Analytical services*

Microanalysis	..	121	samples
VPC analysis	..	310	"
IR analysis	..	231	"
UV analysis	..	66	"
NMR spectra	..	39	"

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

1. Sample of cetyl-stearyl alcohol tested for water evaporation retardatin properties Central Railway Headquarters, Bombay.
2. Three mercury pulse delay units reconditioned. IAF Radar, Poona.
3. Electronic stimulator serviced. B. J. Medical College, Poona.
4. Servicing of Beckman pH-meters; photoelectric calorimeter, (Helige chromatrons model); spectronic-20 calorimeter (Bausch and Lomb). Poona Field Unit, CIPHERI.
5. Photoelectric colorimeter serviced. Sugarcane Research Station, Padegaon, Post Nira.
6. Following samples were analysed and tested:
 - a. Transformer oil Ganeshkhind Power Station, Poona.
 - b. Filtering medium M/s Kirloskar Oil Engines, Poona.
 - c. Ash from sulphur burners M/s Travancore Titanium Products Ltd., Trivendrum.

<i>d.</i> Indium metal for gallium, lead, tin and arsenic contents.	M/s Semiconductors Ltd., Poona.
<i>e.</i> Cutlery alloy	All India Handicrafts Board, Bombay.
<i>f.</i> Tellurium in metallic lead	M/s National Peroxide, Bombay.
<i>g.</i> Graded samples of gypsum for metallic impurities	Physics Dept., Saugar University, Saugar.
<i>h.</i> Mercury in urine	Sassoon Hospitals, Poona.
<i>i.</i> Fluxes for soldering aluminium alloys	MERADO, Poona.
<i>j.</i> Advice based on testing and experiments on beneficiation of barium carbonate	M/s Indian Schering Co., Bombay.
<i>k.</i> Microanalyses for elements and functional groups (121 samples)	Different parties.
<i>l.</i> Complete literature survey for proper methods of estimation of sex hormones	Medical College, Dept. of Ophthalmology, Aligarh University, Aligarh.
<i>m.</i> VPC analyses (311 samples)	Different parties.
<i>n.</i> Analysis of rubber-based damper tube	M/s Sriram Refrigeration Industry, Hyderabad.
<i>o.</i> Physical properties of plastic tubes for use in dam model	Bhakra and Beas Designs Organisation, New Delhi.
<i>p.</i> Analysis of rubber covering on rice mill huller roller	CFTRI, Mysore.
<i>q.</i> Sealing composition for trans-fusion liquid bottles	AFMC, Poona.

- r. Information on substitution of imported lead for jointing GI pipes CIPHERI, Nagpur.
- s. Modifications to overcome the draw-backs in the manufacture of buttons from UF moulding powder M/s Praga Industries, Coimbatore.
- t. Identification of fillers used in moulding powders M/s Indian Plastics Ltd., Bombay.
- u. Design of pilot plant size solvent extraction unit for batch processing of solids Oil Technological Research Institute, Anantpur.
- v. The following fabrication work was carried out in Workshop:
- Thin layer chromatography applicators (one each) .. NBG,Lucknow;CSMCRI,Bhavnagar; Univ. of Poona, Poona and Univ. of Karantak,Dharwar.
- An equipment to prepare dry ice-cake (Snow-man) .. University of Poona, Poona.
- Exhaust blower (fume extractor) .. University of Poona, Poona.
- w. Following glass-blowing work was carried out:
- Solvent extraction unit with complete assembly .. B. J. Medical College, Poona.
- Jacketted columns .. Maharashtra Association of Cultivation of Science, Poona.
- Glass cell as per design .. Dept. of Chemistry, Univ. of Saugar, Saugar.
- Pyrex glass distiller-double stage .. Institute of Tropical Meteorology, Poona.
- Repairing of rotameter glass pipe .. M/s Sandvik Asia Ltd. Poona.
- Air bubbler assembly .. Institute of Tropical Meteorology, Poona.
- Standard ground glass apparatus .. Indian Explosives Ltd., Gomia,
- Fusing of silica tubings .. Semiconductors Ltd., Poona.
- Chromatographic columns with sintered disc and stopcock .. Indian Drugs & Pharamaceuticals Ltd., Virbhadra, (U.P.)

A-III DEMONSTRATIONS

Preparation of ceto-stearyl alcohol	RRL, Hyderabad.
Preparation of water dispersible DDT	M/s Lotus Industries, Madras.
Preparation of stearamide	BTRA, Bombay.
Preparation of rubberised cork sheets	M/s Bharat Casements Pvt. Ltd., Baroda.
Vapour phase chromatograph (proto-type unit.)	M/s Hyderabad Allwyn Metal Works, Hyderabad. M/s Scientific Instruments Co., Bombay.

A-IV PROCESSES LEASED OUT DURING 1966-67

Process	Party	Remarks.
Manufacture of rubberised cork sheet	M/s Bharat Casements Pvt. Ltd., Baroda.	Technical aid against payment, non-exclusive.
Acetanilide	Hindustan Organic Chemicals Ltd. P. O. Rasayani (through M/s R. L. Dalal & Co. Bombay).	Exclusive for M/s Dalal for project engineering.
Dibutyl and dioctyl phthalates	M/s R. L. Dalal & Co. Bombay (project engineers).	Non-exclusive.
Rubber base contact adhesive	M/s Bhagsons & Paint Industries, (India) New Delhi.	Non-exclusive.
Water dispersible DDT as oil bound paste	M/s Lotus Industries, Madras.	Non-exclusive.
Preparation of insoluble reaction products of polystyrene for the use as cation exchange materials	M/s Tulsi Industries, Poona.	Non-exclusive.
Polyurethane printing rollers	M/s United Ink and Varnish Co., Bombay.	Non-exclusive.

Recovery of pyridine bases from their aqueous solutions	M/s Rainbow Tex Dyes, Corpn. Baroda.	Technical aid against payment, non-exclusive.
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A-V SPONSORED PROJECTS COMPLETED DURING 1966-67

Investigation of a fermentation problem	M/s Aphali Pharmaceuticals Ltd., Ahmednagar.
Studies in pine oil from Indian turpentine oil	M/s Prabhat General Agency, Bombay.
Titanium tetrachloride from ilmenite	M/s Travancore Titanium Products Ltd., Trivandrum.
Commercial uses of Punjab costus root (Kuth)	Govt. of Punjab.

A-VI TRAINING

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

Experimental methods in solid state, natural products, VPC techniques, glass blowing, plant tissue culture techniques and microbiological techniques.

A-VII SEMINARS AND LECTURES

Weekly seminars are held at NCL in which members of the scientific staff take an active interest. In addition to the talks by several NCL scientists, the following lectures were delivered by outside eminent scientists at the NCL :—

1. Dr. Ian Dubik, Director, Institute of Inorganic Chemistry, Poland. Scientific research and industry in Poland.
2. Prof. Mohammed Yousseff Saada, UAR Scientist. Two-phase co-current flow.
3. Prof. Brijen K. Gupta, Brooklyn College City University, New York. Planning for science and technology in India.

4. Dr. H. G. Pandit, Hovenkamp, Oxidative phosphorylation in
Laboratorium voor Biochemie, *azotobacteri vinelandii*.
Universiteit van Amsterdam,
Amsterdam.
5. Prof. Wiktor Kemula, Some aspects of polarography.
Academician & Prof. of Chemistry,
Poland.
6. Prof. G. Varsanyi, Head of the Radial skeletal vibrations of
Dept. of Physical Chemistry, benzene derivatives.
Polytechnical University, Budapest.
7. Prof. W. Kern, Principles of ageing of polymers.
University of Mainz, W. Germany.
8. Prof. K. Vedam, Optical properties of solids at high
Pennsylvania State University, pressures.
U.S.A.
9. Dr. C. C. J. Colvenor, CSIRO, Some aspects of the chemistry of
Australia. pyrrolizidine alkaloids.
10. Dr. S. K. K. Jatkar, Poona. Electric and magnetic susceptibili-
ties. Technical applications and
problems. Spin isomers - Part I & II
11. Prof. A. K. Ramdas, Electronic and vibrational spectra
Dept. of Physics, Purdue University, of imperfections in solids.
U.S.A. Piezo-spectroscopic efforts of im-
purity states in semiconductors.
12. Dr. W. Jenny, Ciba Ltd., Basle. Coronaphenes, a new class of hydro-
carbons.
13. Dr. H. C. Freeman, Model compounds for metal-protein
University of Sydney, Australia. interaction: Transition metal
complexes of glycine peptides and
histidine peptides.
14. Dr. N. Blakebrough, Some aspects of biochemical
Birmingham University, U. K. engineering.
15. Dr. G. Rajagopalan, Some recent work on the amino
Rockefeller University, New York. acids sequence determination o-
proteins (pepsin).

- | | |
|---|--|
| 16. Prof. F. C. Happold, Dept. of Biochemistry, University of Leeds, U.K. | The tryptophan story since Hopkins. |
| 17. Prof. E. W. Fischer, University of Mainz, W. Germany. | Theory of melting of semicrystalline polymers. |
| 18. Prof. C. Meyerhoff, University of Mainz, W. Germany. | Determination of molecular weight distributions. |
| 19. Dr. S. V. Mahohar, McGill University, Montreal, Canada. | Nucleotide metabolism in red blood cells. |
| 20. Dr. D. R. Sanadi, Dept. of Bioenergetics Research Retina Foundation, Boston, U.S.A. | Energy metabolism of cell. |
| 21. Prof. Dorothy Hodgkin, FRS, N. L., University of Oxford, U.K. | Structure elucidation of vitamin B ₁₂ by X-ray crystallography. |

Ten NCL scientists delivered more than 15 scientific lectures on different subjects at various research institutes and universities in the country.

A-VIII STAFF NEWS

1. *Foreign deputations/training etc.*

Dr. A. B. Deshpande proceeded to Japan under Colombo Plan for 'Studies in polymers' for one year (April 1966).

Mr. V. S. Krishnamachar returned from Canada after receiving training under Colombo Plan in the field of microbiology with respect to maintenance of microorganisms (November 1966).

Mr. A. D. Deshpande proceeded to France under Indo-French Cooperation agreement for training in 'Advance techniques in the field of applied research in chemical engineering' for a period of one year (June 1966).

Dr. Sukh Dev participated in the International Symposium on 'Natural products' held at Stockholm, Sweden (June-July 1966).

Mr. S. H. Iqbal returned from France after receiving training in the 'Chemistry of titanium compounds' under the French Govt. scholarship (August 1966).

Mr. Koli, S. S.	Ph. D.	Poona
Mr. Koul, B. L.	Ph. D.	Bombay
Mr. Krishnamurthy, B. S.	Ph. D.	Poona
Mr. Mathur, S. B.	Ph. D.	Poona
Mr. Menzies, C. A.	Ph. D.	Poona
Mr. Narsimhan, K. S. V. L.	Ph. D.	Poona
Mr. Navangul, H. V.	Ph. D.	Poona
Mr. Pachhapurkar, R. V.	Ph. D.	Poona
Mrs. Patwardhan, S. V.	Ph. D.	Bombay
Mr. Patil, J. R.	Ph. D.	Poona
Mr. Radhakrishnan, P. V.	Ph. D.	Bombay
Mr. Sakore, T. D.	Ph. D.	Poona
Mr. Saxena, P. C.	Ph. D.	Poona
Miss Sayagavar, H. M.	M. Sc.	Bombay
Mr. Sharma, P. G.	Ph. D.	Poona
Mr. Srivastava, K. C.	Ph. D.	Poona
Mr. Shukla, O. P.	Ph. D.	Poona

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

Dr. Bhattacharyya, S. C.	Poona, Bombay, Calcutta, Agra, Vikram, Banaras.
Dr. Biswas, A. B.	Poona, Bombay, Punjab, Andhra, Calcutta, Karnatak, Banaras.
Dr. Bose, J. L.	Bombay, Poona, Nagpur.
Dr. Chakravarti, K. K.	Bombay, Poona, Shivaji.
Dr. Dadape, V. V.	Bombay, Poona, Karnatak, Vikram, Banaras.
Dr. Damodaran, V.	Sri Venkateshwar University, Tirupathi.
Dr. Doraiswamy, L. K.	Poona, Bombay, Nagpur, Banaras, Calcutta, Jadavpur.
Dr. Dutta, N. L.	Poona.
Dr. Ghatge, N. D.	Poona, Bombay, Shivaji.
Dr. Goswami, A.	Calcutta, Poona, Punjab.
Dr. Gupta, J.	Bombay, Poona, Punjab, Madras.
Dr. Jagannathan, V.	Bombay, Poona.
Dr. Kapur, S. L.	Bombay, Poona, Punjab, Madras.
Dr. Katti, S. S.	Bombay.
Dr. Kelkar, G. R.	Poona.
Dr. Kulkarni (Miss), S. B.	Poona.
Dr. Kulkarni, S. N.	Poona, Bombay, Karnatak.
Dr. Mathur, H. B.	Poona, Agra, Madras.

Dr. Narayanan, C. R.	Poona, Bombay.
Dr. Nair, P. M.	Poona.
Dr. Pai, M. U.	Bombay.
Dr. Pant, L. M.	Poona.
Dr. Rao, A. S.	Poona, Bombay.
Dr. Rao, M. R. R.	Bombay, Poona.
Dr. Sadana, J. C.	Poona.
Dr. Sen, D. N.	Poona, Bombay.
Dr. Sinha, A. P. B.	Poona, Banaras, Vikram, Karnatak.
Dr. Sinha, K. P.	Poona, Agra, Bombay.
Dr. Sivaraman, C.	Poona.
Dr. Subbaraman, P. R.	Poona, Bombay, Gujarat, Kerala.
Dr. Sukh Dev	Poona, Bombay, Agra, Punjab, I. I. Sc., Bangalore.
Dr. Tilak, B. D.	Bombay, Poona.
Dr. Venkataraman, K.	Poona, Bombay, Madras, Banaras.

A-IX PUBLICATIONS

Research papers

1. Rao, R. V. G., Subba Rao, V. V. and Biswas, A. B.
Thermal decomposition of neodymium oxalate and changes in surface areas of the products.
J. Inorg. Nucl. Chem. **28**, 415 (1966).
2. Jain, S. C., Tavale, S. S., and Biswas, A. B.
On the crystal structure of some α -oxoacids.
Collected Abstract of 7th International Congress and Symposium on Crystal Growth, Moscow, (USSR), A 124, (1966).
3. Pant, L. M., Sakore, T. D. and Biswas, A. B.
The structure of nickel imidazole nitrate dihydrate.
Collected Abstract of 7th International Congress and Symposium on Crystal Growth, Moscow, (USSR), A 158, (1966).
4. Sabane, C. D., Sinha, A. P. B. and Biswas, A. B.
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Indian J. Pure Appl. Phys. **4**, 187 (1966).
5. Chavan, A. M., Dhut, R. M., Lakbir Singh and Biswas, A. B.
Thermogravimetric study of the reduction of co-precipitated nickel copper carbonates.
Indian J. Chem. **4**, 211 (1966).

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Ultrasonic degradation of macromolecules in solution. A study of degradation kinetics by estimation of free radical scavenger DPPH and solution viscosity measurements.
J. Appl. Polymer Science **10**, 1089 (1966).
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On the crystal structures of α -oxoacids.
Acta Cryst. **21**, 445 (1966).
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12. Ganguly (Mrs), Leela., Jose, C. I. and Biswas, A. B.
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Spectrochim Acta **23A**, 513 (1967).
13. Jose, C. I. and Pabrai, P. R.
Intramolecular hydrogen bonding of substituted acetyl ureas in solution.
Spectrochim Acta **23A**, 734 (1967).
14. Sakore, T. D. and Pant, L. M.
The structure of *p*-nitrobenzoic acid.
Acta Cryst. **21**, 715 (1966).
15. Ranade, A. C. and Subba Rao, V. V.
Magnetic susceptibilities of some first row transition metal carboxylates.
Indian J. Chem. **4**, 42 (1966).

16. Joshi, A. W. and Sinha, K. P.
Low temperature thermal conductivity of ferrimagnetic insulators.
Proc. Phys. Soc. (London), **88**, 685 (1966).
17. Ganguly, B. N., Upadhyaya, U. N. and Sinha, K. P.
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Indian J. Chem. **4**, 94 (1966).
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Resorcin 2:4 -dialdehyde and some of its chelate polymers.
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Bakuchiol, a novel monoterpenoid.
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Studies in sesquiterpenes XXV—A synthesis of β -selinene.
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Studies in sesquiterpenes XXVI—Synthesis of 2,2,6-trimethyl-3-oxo-1-carbomethoxy-bicyclo(0,3,3)octane, a degradation product of patchouli alcohol.
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Photochemistry of zerumbone.
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Lac pigments.
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Electron impact studies I—Skeletal rearrangements of semicarbazones and thiosemicarbazones.
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Macrocyclic musk compounds.
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chemistry of (—) santonin and solid dihydrocostunolides at C II.
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Bhattacharyya, S. C.
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oxidation with lead tetraacetate.
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and transformation of 1α , 5α , dihydroguaiol to 1α , 5α ,
hexahydrodehydrocostus lactone.
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Bhattacharyya, S. C.
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khusinol oxide, a new antipodal sesquiterpene epoxy alcohol from
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Bhattacharyya, S. C.
Terpenoids CIII—Synthesis of santanolide 'C',
tetrahydroalantolactone, lactone of β -hydroxyeudesman-15-oic acid
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A-X PATENTS IN FORCE

Patents sealed

1. **45666**
Manufacture of nicotine sulphate from tobacco waste.
Gedeon, J. and Goswami, M.
2. **47433**
A process for the manufacture of a mixed N. P. fertilizer.
Gadre, G. T. and Gupta, J.
3. **53636**
Improvements in or relating to coating compositions.
Sarin, K. K. and Kapur, S. L.
4. **54867**
A process for the manufacture of nicotine sulphate from tobacco and tobacco wastes.
Bijawat, H. C., Razdan, R. and Potnis, G. V.
5. **55171**
Treatment of CNSL for use in electrical insulating varnishes.
Thakar, K. G. and Gupta, J.
6. **55546**
Improvements in or relating to ion exchange materials.
Ramakrishnan, C. S. and Krishnaswamy, N.
7. **56725**
A new process for the purification of selenium.
Sen, D. N. and Gupta, J.
8. **56726**
Preparation of water dispersible DDT as an oil bound paste.
Rao, K. V. N., Bhide, S. P. and Kulkarni (Miss), S. B.
9. **57888**
Improvements in or relating to the production of hydroxy, alkoxy or aryloxy substituted aryl alkyl ketones.
Bose, J. L. and Shah, R. C.

10. **58868**
A process for the preparation of azelaic acid semiester suitable for making civetone dicarboxylic acid.
Nayak, U. G., Chakravarti, K. K. and Bhattacharyya, S. C.
11. **59419**
A process for the preparation of tridecane 1:13 dicarboxylic acid or its ester, suitable for the preparation of exaltone (cyclopentadecanone).
Ghatge, B. B. , Nayak, U. G., Chakravarti, K. K. and Bhattacharyya, S. C.
12. **59497**
Production of porous ploymer suitable for preparing cation exchange resins.
Govindan, K. P., Pandya, R. N. and Krishnaswamy, N.
13. **59606**
Preparation of cation exchange resin from porous cashewnut shell liquid polymer.
Krishnaswamy, N., Pandya, R. N. and Govindan, K. P.
14. **59608**
Rigid filters.
Kapur, S. L. and Pandya, R. N.
15. **59853**
Improvements in or relating to the preparation of costus root oil and the isolation of lactonic constituents therefrom.
Kelkar, G. R. and Bhattacharyya, S. C.
16. **59927**
A process for the preparation of pentadecane 1:15-dicarboxylic acid or its ester suitable for the preparation of dihydrocivetone.
Nayak, U. G., Chakravarti, K. K. and Bhattacharyya, S. C.
17. **60555**
Production of liquid rubber.
Uma Shankar.

18. **60826**
Improvements in or relating to the production of hydroxy, alkoxy or aryloxy substituted deoxybenzoins and particularly of deoxyanisoin.
Bose, J. L. and Shah, R. C.
19. **61585**
A process for the manufacture of an ammonium phosphate-sulphate fertilizer.
Gupta, J., Sheshadri, K., Lobo, J. and Rao, M. N.
20. **62890**
A new process for the production of 4-hydroxycoumarin and its derivatives.
Shah, V. R., Bose, J. L. and Shah, R. C.
21. **63083**
A new method for the preparation of 4-hydroxycoumarins.
Shah, V. R., Bose, J. L. and Shah, R. C.
22. **64958**
Improvements in or relating to polishing compositions.
Shah, S. M., Hinge, V. K., Mhaskar, V. V. and Shah, R. C.
23. **64959**
A process for the preparation of dihydrojasnone.
Amin, J. H. and Bhattacharyya, S. C.
24. **65440**
A process for the extraction of wax from sisal waste.
Shah, S. M., Hinge, V. K., Mhaskar, V. V. and Shah, R. C.
25. **65543**
A process for the preparation of ω -dicarboxylic acids and ω -hydroxy acids suitable for conversion to macrocyclic compounds.
Mathur, H. H. and Bhattacharyya, S. C.
26. **65777**
A new process for the production of 4-hydroxycarbostyrils.
Shah, V. R., Bose, J. L. and Shah, R. C.

27. **65778**
Improvements in or relating to the production of transdiethylstilbestrol dimethyl ether and allied stilbenes.
Joshi, C. G., Bose, J. L. and Shah, R. C.
28. **65976**
Improvements in or relating to the suspension polymerization of vinyl monomers.
Joshi, R. M. and Kapur, S. L.
29. **65977**
Rubber-base adhesive.
Uma Shankar.
30. **66096**
A process for the production of bacterial diastase by submerged culture.
Babbar, I. J., Bekhi, R. M. and Srinivasan, M. C.
31. **66194**
Improvements in or relating to can sealing composition.
Raghunath, D. and Kapur, S. L.
32. **66803**
Improvements in or relating to the manufacture of pressure sensitive adhesive tapes.
Kapur, S. L. and Rao, B. R. K.
33. **66836**
Manufacture of ethylene dichloride.
Banerjee, S. C., Phatak, S. L., Pai, M. U. and Doraiswamy, L. K.
34. **66966**
An improved process for the production of porous rigid filters.
Kapur, S. L. and Pandya, R. N.
35. **67490**
Preparation of adhesive tapes.
Kapur, S. L. and Rao, B. R. K.

36. **67513**
Improvements in or relating to the separation of niobium and tantalum from each other by liquid-liquid extraction.
Sarma, B. and Gupta, J.
37. **68611**
A new device for generating electrical power from the atmosphere.
Momin, A. U.
38. **70670**
Improvements in or relating to the controlling of water evaporation for conserving of water in lakes and reservoirs.
Kulkarni (Miss), S. B., Gharpurey, M. K., Deo, A. V., Sanjana, N. R., Abraham, K. P. and Subba Rao, B. C.
39. **71063**
Production of bacterial protease by submerged culture.
Babbar, I. J., Powar, V. K. and Jagannathan, V.
40. **71190**
Preparation of anion exchange resins.
Krishnaswamy, N., Govindan, K. P. and Dasare, B. D.
41. **72425**
A direct process for preparing the chlorides of barium and strontium from their sulphate minerals.
Iqbal, S. H., Lobo, J. and Gupta, J.
42. **73702**
A process for the preparation of cyclopentadecanolide (exaltolide).
Dhekne, V. V., Ghatge, B. B. and Bhattacharyya, S. C.
43. **74356**
Preparation of insoluble reaction products of polystyrene for use as cation exchange materials.
Govindan, K. P. and Krishnaswamy, N.
44. **74451**
Preparation of covering materials from anacardic materials.
Raghunath, D., Suryanarayana, N. P. and Krishnaswamy, N.

45. **77080**
A process for preparation of ambrettolide.
Sabnis, S. D., Mathur, H. H. and Bhattacharyya, S. C.
46. **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.
47. **77224**
Synthetic esters as speciality lubricants for low temperature performance and particularly for the lubrication of clocks and watches.
Pathak, K. D. and Subba Rao, B. C.
48. **77225**
A process for the preparation of β -ionone from pseudoionone.
Joshi, B. N., Chakravarti, K. K., Shah, R. C. and Bhattacharyya, S. C.
49. **82189**
Production of dextro-tartaric and oxalic acids.
Vartak, H. G., Patil, S. G. and Jagannathan, V.
50. **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.
51. **83364**
Manufacture of hexachloroethane.
Bhat, N. A., Goswami, M. and Pai, M. U.
52. **83716**
Manufacture of nicotine sulphate from tobacco and tobacco wastes.
Potnis, G. V., Goswami, M., Ramachandran, V. and Pai, M. U.
53. **85446**
Preparation of carboxylic cation exchange materials.
Krishnaswamy, N., Indusekhar, V. V. and Dasare, B. D.

54. **85789**
Utilization of groundnut shells for the manufacture of high alpha cellulose dissolving grade pulp.
Vyas, G. M., Bendale, D. S., Mahajan, M. B., Bose, J. L., Modi, B. D., Sonawane, H. R. and Bigg, D. C.
55. **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.
56. **86638**
A process for the preparation and synthesis of 2-*iso*-propenyl hexanols.
Ramaswami (Mrs.), S., Ramaswami, S. K. and Bhattacharyya, S. C.
57. **86991**
Preparation of polyurethane printing rollers.
Ghatge, N. D. and Kapur, S. L.
58. **89004**
A polycrystalline p-n junction photovoltaic solar cells.
Momin, A. U. and Sinha, A. P. B.
59. **90574**
A process for the preparation of *dl*-muscone.
Nair, M. S. R., Mathur, H. H. and Bhattacharyya, S. C.
60. **95075**
Utilization of groundnut shells for the manufacture of vanillin.
Vyas, G. M., Bendale, D. S., Mahajan, M. B., Bose, J. L., Modi, B. D., Sonawane, H. R. and Bigg, D. C.
61. **95076**
Improvements in or relating to the manufacture of lignin.
Vyas, G. M., Bendale, D. S., Mahajan, M. B., Bose, J. L., Modi, B. D., Sonawane, H. R. and Bigg, D. C.

Patents filed

1. **81071**
Improvements in or relating to the recovery of nickel and fat from spent nickel hydrogenation catalyst.
Murthy, M. N. S. and Biswas, A. B.

2. **81072**
Improvements in or relating to the preparation and production of catalysts for the hydrogenation of organic substances with particular reference to fatty oils.
Murthy, M. N. S., Biswas, A. B.
3. **90677**
A new method for the preparation of formic acid.
Vartak, H. G., Patil, S. G. and Paranjape, S. V.
4. **91412**
Manufacture of 2,3-hydroxynaphthoic acid from 2-naphthol.
Phadtare, P. G., Srinivasan, K. R., Baliga, B. A.,
Kotasthane, M. G. and Doraiswamy, L. K.
5. **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.
6. **64766**
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.
7. **96663**
A new process for the manufacture of glycolic acid.
Vartak, H. G. and Patil, S. G.
8. **96801**
A new method for the improvements in the figure of merit of thermoelectric material.
Narsimhan, K. S. V. L. and Sinha, K. P.
9. **97190**
Improvements in or relating to extractors for extraction or similar processes.
Narsimhan, G. and Shah, C. M.
10. **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.

11. **98156**
Preparation of solvent modified copolymers of vinyl monomers in bead form.
Kapur, S. L. and Ramkrishnan, K.
12. **99589**
A process for the preparation of benzoyl chloride.
Aggarwal, K. L. and Doraiswamy, L. K.
13. **99590**
Process for the manufacture of a novel binding agent for core sand.
Varma, J. P.
14. **101161**
Process for the preparation of day light and pink light emitting electro-luminescent phosphors.
Ambardekar, D. S. and Biswas, A. B.
15. **106804**
Improvement related to the manufacture of carboxy methyl cellulose.
Bendale, D. S., Mahajan, M. B. and Khadilkar, H. P.
16. **106808**
Improvements in or relating to the preparation of mixed oxide ceramic compositions.
Murthy, M. N. S. and Sinha, K. P. B.
17. **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.
18. **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.
19. **109006**
A modified process for the preparation of expandable thermoplastic beads.
Kapur, S. L. and Sehra, J. C.
20. **109489**
Production of aryl-glycosides.
Ingle, T. R. and Bose, J. L.

PROCESSES IN PRODUCTION

S.No.	Name of the process and year of commencement of production	Field of utilization	Name of the manufacturer	Production & value (1966-67)	Remarks
1	2	3	4	5	6
1.	Anion exchange resin from melamine (1963)	Demineralization of liquids	M/s Tulsi Industries, Poona.	44 cft. Rs. 13,200/-	Production upto March 1966- 4 cfts, value Rs. 872/-
2.	Antipriming compositions (sponsored) (1964)	Antipriming in locomotives	Research Designs and Standards Organization, Min. of Railways, Chittaranjan.	22,000 Kg. Rs. 52,000/-	Production upto March 1966— 18,600 kg., value Rs. 27,000/-
3.	Berberine hydrochloride (sponsored) (1965)	Pharmaceuticals	M/s G. Vallabhdas & Co., Bombay.	*	Production upto March 1966— 300 kg., value Rs. 36,000/-
4.	Can sealing composition (1962)	Metal can industry	M/S Arya Chemical Works, Calcutta.	18,500 kg. Rs. 1,00,000/-	Production upto March 1966— 53,000 kg., value Rs. 2,72,000/-

1	2	3	4	5	6
5.	Cation exchange resin from CNSL (1960)	Demineralization of liquids	M/s Tulsi Industries, Poona-5.	300 cft. Rs. 35,200/-	Production upto March 1966— 7,800 cft., value Rs. 5,52,000/-
6.	Dihydroisojasmone and peach aldehyde (1965)	Perfumery	M/s S. H. Kelkar & Co., Bombay.	*	Experimental production established, production irregular for want of market.
7.	Ethylene oxide condensates (sponsored) (1965)	Surface active agents	M/s Hico Products Ltd., Bombay.	1,60,800 kg. Rs. 19,24,000/-	Production figure quoted for 1966.
8.	Heat sealable coating compositions (Tech. aid) (1963)	Adhesive for film waste	M/s Chandmal Fakirchand Jain, Indore.	*	Reported to be in production.
9.	Hexylresorcinol (1964)	Pharmaceuticals	M/s Unichem Laboratories, Bombay.	*	Production upto March 1966— 13 kg., value Rs. 7,800/-
10.	4-Hydroxycoumarin and warfarin (1964)	Pharmaceuticals, antirodent	M/s Unichem Laboratories, Bombay.	*	Production upto March 1966— 47 kg., value Rs. 11,400/-

1	2	3	4	5	6
11.	β-Ionone (1964)	Perfumery, pharmaceuticals	M/s S. H. Kelkar & Co., Bombay.	*	Experimental production established, production ir- regular for want of market.
12.	Liquid rubber (1962)	Adhesives	M/s K. N. Chari & Co., Madras.	*	Production up to March 1966— 2200 kg., product manufactured for captive use.
13.	Nicotine sulphate (1963)	Insecticides	M/s Patel & Co., Dharmaj, (Gujarat)	3600 kg. Rs. 68,000/-	Production upto March 1966-- 6700 kg., value Rs. 50,500/-
14.	Polyurethane printing rollers (1965)	Printing	M/s Saraswathy Press P. Ltd., Calcutta.	*	Experimental production established.
15.	Rigid filters (1965)	Tube wells	M/s Ashim Filters, New Delhi.	753 mtrs. Rs. 1,27,000/-	Production upto March 1966— 53 mtrs., value Rs. 7,800/-
16.	Rubber base contact adhesive (1962)	Adhesives	M/s K. N. Chari & Co., Madras.	846 litres Rs. 3584/-	Production upto March 1966— 12,200 litres, value Rs. 1,13,000/-
17.	Rubberised cork sheet (Tech. aid) (1966)	Gaskets	M/s Bharat Casements P. Ltd., Baroda.	*	Reported to be in production.

1	2	3	4	5	6
18.	Silica gel (sponsored) (1963)	Humidity control	M/s Minco Products, Madras.	9900 kg. Rs. 83,000/-	Production upto March 1966— 27,300 kg., value Rs. 1,13,000/-
19.	Sisal wax (1962)	Cosmetics, polishes	M/s Aphali Pharmaceuticals Ltd., Ahmednagar.	*	Production upto March 1966— 14,200 kg., value Rs. 1,53,200/-
20.	Tetrabromoindigo (sponsored) (1966)	Dye intermediate	M/s Shree Dyes, Poona.	*	Reported to be in production.
21.	Thermistors (Tech. aid) (1963)	Electronic devices	M/s Semiconductors Pvt. Ltd., Poona.	4,09,700 pcs. Rs. 5,30,000/-	Production upto March 1966— 4,92,800 pcs., value Rs. 6,50,000/-
22.	Utilization of by-products of DDT factory (sponsored) (1966)	Chemicals	M/s Hindustan Insecticides Ltd., New Delhi.	4600 kg. Rs. 37,000/-	Production figure relates to the manufacture of chloral hydrate B. P., export of chloral hydrate (1966-67) was \$ 840. Production upto March 1966— 37,000 kg.

1	2	3	4	5	6
23.	Water dispersible DDT (1963)	Insecticides	M/s South India Research Institute, Vijaywada.	4600 kg. Rs. 32,000/-	Production upto March 1966— 14,200 kg., value Rs. 95,000/-
<i>Processes in production in Fine Chemicals Project in N. C. L.</i>					
24.	Chromatographic alumina	Laboratory chemicals		1000 kg. Rs. 44,700/-	
25.	Chromatographic silica gel	Laboratory chemicals		600 kg. Rs. 37,000/-	
26.	Phenoxyacetic acid	Pharmaceutical industry		3300 kg. Rs. 41,200/-	

* Attempts are being made to collect up-to-date data from the respective firms.

A-XII

PROCESSES RELEASED AND AWAITING PRODUCTION

S. No.	Process/year of release	Field of utilization	Name of the party	Nature of licence/proposed production/present state of development
1	2	3	4	5
1.	Acetanilide (1966)	Dyestuff intermediate	M/s. R. L. Dalal & Co. Bombay (project engineers).	Exclusive; 2000 T/annum, valued at Rs. 1 crore. Plant selected by Hindustan Organic Chemicals Ltd., Rasayani from among world tenders.
2.	Bacterial diastase (1959)	Textile desizing	M/s Chemaux Pvt. Ltd., Bombay.	Exclusive; 400 T/annum, valued at Rs. 16 lakhs. Erection of the plant completed. Trial runs are in progress with the active help of NCL scientists.
3.	Cation exchange resin (1965)	Deminerlization of liquids	M/s Tulsi Industries, Poona.	Non-exclusive. *
4.	Covering materials from CNSL (1964)	Chemically resistant flooring	M/s Natson Manufacturing Co., Ahmedabad.	Exclusive. Equipment is being procured.

1	2	3	4	5
5.	Diethylstilbestrol (1965)	Pharmaceuticals	M/s Gluconate Ltd., Calcutta.	Exclusive; 70 kg./annum. Efforts being made to procure high pressure equipment. Production will be undertaken on its receipt.
6.	Dioctyl and dibutyl phthalates (1966)	Plasticizers	M/s R. L. Dalal & Co., Bombay (project engineers).	Non-exclusive; the firm is offering turn-key plants of 1500-10,000 T/annum capacity to industry.
7.	Ethyl acetoacetate (1963)	Dyestuff intermediate	1. Indian Organic Chemicals Ltd., Khopoli. 2. M/s Aceto Chemicals Ltd., Calcutta.	Non-exclusive; the firm has already tried the process on large scale semicommercial plant. Pilot plant of 20 kg./day set up. Trials being taken up. Production of 250-500 kg. / day proposed.
8.	Opium alkaloids (1966)	Pharmaceuticals	Ministry of Finance, Govt. of India.	Exclusive; 4.7 T/annum S. R. Morphine valued at Rs. 1 crore. Foundation stone of the proposed factory laid on 12.11.66. Factory scheduled to go on stream in 1970.

1	2	3	4	5
9.	Styrene DVB-base cation exchange resin (1963)	Demineralization of liquids	1. M/s Industrial & Agrl. Engg. Co. P. Ltd., Bombay. 2. M/s Tulsi Industries, Poona. 3. M/s Bird & Co. Ltd., Calcutta.	Non-exclusive; 100 litres/day. Trial production in progress. * *
10.	Titanium tetrachloride (sponsored) (1967)	Industrial chemicals	M/s Travancore Titanium Products Ltd., Trivandrum.	Exclusive; 150 T/annum, valued at Rs. 4,50,000/-. Plant under erection; likely to go on stream by the end of 1967.
11.	Vitamin C (1966)	Pharmaceuticals	Hindustan Antibiotics Ltd., Pimpri, Poona.	Exclusive; 125 T/annum. Large scale pilot plant trials completed. Plant designs prepared by HAL.
<i>Sponsored processes completed</i>				
12.	Acriflavine (1966)	Pharmaceuticals	M/s Bhaidas Karasandas, Bombay.	Complete project report submitted. *
13.	Diethyl- <i>m</i> -aminophenol (1966)	Dyestuff intermediate	M/s Sahyadri Dyestuffs & Chemicals P. Ltd., Poona.	60 T/annum; installation of the plant is expected by the end of 1967.

1	2	3	4	5
14.	Fermentation problem (1966)	Pharmaceuticals	M/s Aphali Pharmaceuticals Ltd., Ahmednagar.	Complete project report submitted. This is an improvement of the existing process.
15.	Reactive dyes (1966)	Dyestuffs	M/s Amar Dye Chem, Bombay.	Complete project report submitted. *
16.	Studies in pine oil (1966)	Industrial chemicals	M/s Prabhat General Agency, Bombay.	Complete project report submitted. The project was of testing nature.
17.	Thiodiglycol (1961)	Dyestuffs	M/s Hico Products, Pvt. Ltd., Bombay.	Not producing at present for economic reasons.
18.	Vat Golden Yellow GK (1966)	Dyestuffs	M/s Amar Dye Chem, Bombay.	Complete project report submitted. *

Following processes which have been mentioned under the table 'Processes in production' are also licensed to the following additional firms.

19.	Liquid rubber (1962)	Adhesives	M/s Swastik Rubber Products Ltd., Kirkee, Poona.	Non-exclusive. *
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1	2	3	4	5	
20.	Nicotine sulphate	Insecticides	1. M/s National Tobacco By-products, Saharanpur. (1963) 2. M/s M. M. Patel, Sunav. (1963) 3. M/s Tobacco By-products, Guntur. (1963)	Non-exclusive. Non-exclusive. Non-exclusive.	* * *
21.	Sisal wax (1966)	Cosmetics, polishes	M/s Shalimar Rope Works, Calcutta.	Non-exclusive.	*
22.	Thermistors (Tech. aid) (1963)	Electronic devices	1. M/s Adept Laboratories, Poona. 2. M/s Tempo Industries Corp., Bombay.	Non-exclusive. Non-exclusive.	* *
23.	Water dispersible DDT (1963)	Insecticides	M/s Pesticides Ltd., Bombay.	Non-exclusive.	

* Attempts are being made to collect up-to-date data from the respective firms

A-XIII

RESEARCH PROJECTS UNDER EVALUATION

S.No.	Name of the process	Field of utilization	Remarks
1	2	3	4
1.	Adhesive for staple pins	Stationery	Process standardized on 5 litres/batch scale. Product approved by industry.
2.	Aniline	Industrial chemical	Turn-key plant will be offered after completion of trial runs.
3.	BON acid	Dyestuff intermediate	Process standardized on 3 kg./batch scale (solvent process). Process and design data for 80 T/annum plant available.
4.	Cadmium sulphide photoconducting cell	Control devices in industry	The cell compares well with the similar imported sample. Circuitry for applications developed. To be evaluated on large scale.
5.	Carbon tetrachloride and chloroform from methane	Industrial chemical, fumigant, refrigeration chemical	Process standardized on 2.5 kg./hr. plant. Further work to be done in collaboration with industry.
6.	Chlorides of barium and strontium	Industrial chemical	One step process standardized on laboratory scale. Large scale work to be done in collaboration with industry.
7.	Core binder (sinol-type)	Foundry chemical	Process standardized on 5 kg./batch scale. Products approved by consumers. Process available to industry.

1	2	3	4
8.	Costus root oil	Perfumery	Process standardized on 50 kg. of roots per batch. Demand in the country is small although there is an export market. Product approved by perfumery houses abroad. Process available to industry.
9.	Diethyl and dimethyl phthalates	Plasticizers	Process standardized on 25 kg./batch scale. Plant designs for 1500 T/annum offered to industry.
10.	Diethyl- <i>m</i> -toluamide	Insect repellent	Process standardized on 0.1 kg./hr. scale. Product approved by AFMC, Poona. Field trials to be taken.
11.	Dimethylaniline	Industrial chemical	Process standardized on 9 kg./batch scale. Process and design data on 600 T/annum offered to industry.
12.	2,4-Dinitromonomethyl-aniline	Intermediate for explosive	Prepared on 50 kg./batch scale. Product tested and found satisfactory.
13.	Dithranol	Antidermatatic agent	Process standardized on 1.5 kg./batch scale. Process data available.
14.	Double boiled linseed oil substitute	Foundry chemical	Composition prepared on 100 kg./batch scale. Field trials successful. Process offered to industry.
15.	Ethylene dichloride	Industrial solvent, chemical intermediate, component of fumigation mixture	Process standardized on 3 kg./hr. scale. Plant designs for 1000 T/annum available.

1	2	3	4
16.	Ferrites (hard and soft)	Audio and high frequency instruments	Compositions of high figure of merit standardized on laboratory scale. Process data offered to industry.
17.	Ferroelectric compositions	Detonators, transducers	Compositions prepared on laboratory scale.
18.	Hexachloroethane	Industrial chemical	Process for manufacture of 500 T/annum offered to industry.
19.	4-Hydroxycarbostyrils	Dyestuff intermediate	Process standardized on laboratory scale. Data offered to industry.
20.	Isocyanate-based adhesive	Water-proofing	Process standardized on laboratory scale.
21.	Lanolin (B. P.)	Cosmetics, pharmaceuticals	Process standardized on laboratory scale. Samples approved by industry.
22.	Luminescent materials	Luminescent paints for fluorescent tubes	Process standardized on laboratory scale.
23.	<i>para</i> -Menthane hydroperoxide	Catalyst for styrene-butadiene copolymerization	Process standardized on 5 kg./batch scale.
24.	<i>d</i> - and <i>dl</i> -menthol from citronellal	Pharmaceuticals	Process standardized on laboratory scale.

1	2	3	4
25.	Modified sugarcane wax	Polishing compositions	Process standardized on 5 kg./batch scale.
26.	Monoethylaniline	Dyestuff intermediate	Process standardized on 3-4 kg./hr. scale.
27.	Perfumery and aromatic chemicals (Civetone, Dihydrocivetone, Dihydrojasmone, Dihydroambrettolide and Isoambrettolide, Exaltone and Exaltolide, Neolavandulol)	Perfumery	Demand in the country for these chemicals is very small. Products approved by consumers. Processes standardized on laboratory scale (approx. 1 kg./batch) and available to industry.
28.	Polycaprolactum powder for chromatography	Laboratory chemicals	30 kg. were prepared and used in the laboratory. Production envisaged in FCP.
29.	Sealants for canvas water bags	Water-proofing	Process standardized on laboratory scale.
30.	Silicon tetrachloride	Silicones, rubber	Process standardized on laboratory scale.
31.	Sorbitol	Vitamin C production, humectant, pharmaceuticals	Process standardized on 10 kg./batch scale.

1	2	3	4
32.	Styrenated alkyds	Surface coatings	Process standardized on 10 litres/batch scale. Product approved by industry.
33.	Styrene DVB-base anion exchange resin	Demineralization of liquids	Process standardized on 15 kg./batch scale (polymerization step) and 2.5 kg./batch scale (amination step). Process data offered to industry. Accepted by one firm.
34.	<i>o</i> -Tolylbiguanide (Sopanox)	Antioxidant for soaps	Process standardized on laboratory scale.
35.	Vanadium catalyst	Sulphuric acid manufacture	Process standardized on 30 litres/batch scale.
36.	Vapour phase chromatograph (proto-type unit)	Instrumental analysis	Design and know-how for fabrication offered to industry.
37.	Vitamin B ₆	Pharmaceuticals	Conventional process standardized on laboratory scale. Modifications in the process are in view.

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