

NATIONAL CHEMICAL LABORATORY

POONA 8

HALF YEARLY REPORT

April-September 1965

NATIONAL CHEMICAL LABORATORY

Poona-8

Half-yearly report

April 1965 to September 1965

C O N T E N T S

<u>S.No.</u>		<u>Page</u>
1.	INTRODUCTION - SUMMARY OF THE MAIN ACHIEVEMENTS	i
2.	PILOT PLANT PROJECTS	1
3.	SPONSORED PROJECTS	7
4.	RESEARCH PROJECTS AND SCHEMES	17
	Physics and Chemistry of Solids	17
	Solution Chemistry	33
	Radiation and Nuclear Chemistry	34
	Catalysis	36
	Physical Chemistry of Macromolecules	37
	Rare Metal Chemistry	38
	Coordination Compounds and Synthetic Inorganic Chemistry	40
	Physicoanalytical Chemistry	43
	Fluorine Chemistry	45
	High Temperature Chemistry	46
	Natural Organic Products	47
	Organic Reactions and Synthesis	54
	Physical Organic Chemistry	66
	Biochemistry	67
	Polymer Chemistry	80
	Chemical Engineering Studies	91
5.	OPERATIONAL RESEARCH, INDUSTRIAL LIAISON AND EXTENSION	99
6.	PUBLICATIONS AND PATENTS	106
7.	LIBRARY HOLDINGS, NEW ADDITIONS	111
8.	SEMINARS, SYMPOSIA AND EXHIBITION	112
9.	VISITORS	114
10.	ADMINISTRATION	114
11.	NEW APPOINTMENTS/RESIGNATIONS/	117
12.	FOREIGN DEPUTATIONS/AWARDS/HONOURS/FELLOWSHIPS, etc.	117
13.	AID UNDER UN SPECIAL FUND/COLOMBO PLAN, PL-480, etc.	120

1. INTRODUCTION
Summary of the
Main Achievements

Pilot Plant Projects

During the period under review, work on seven pilot plant projects was in progress. In Fine Chemicals Project, production of phenoxy acetic acid, 25 kg./batch and malonic acid, 10 kg./batch and a laboratory preparation of sorbic acid has been established. From the comparative study of different pulping processes, it is found that acid prehydrolysis sulphate process and two stage alkali process are suitable for Melocanna-bamboo species, received from the Director of Industries, Tripura. Upgraded ilmenite ore has been chlorinated in 6" dia refractory tube reactors and an optimum rate of 1 kg. of $TiCl_4$ /hour has been achieved. $TiCl_4$ has been further hydrolysed to pigment grade rutile titania on 1 kg. scale. A multitubular type reactor for hydrogenation of nitrobenzene to aniline has been set up. It is found that the catalyst remains active even after 800 hours of use. A batch process producing 8-10 kg. of dimethylaniline per batch has been developed. Work is in progress to optimise the conditions for the production of tetrachloroethane from ethylene with the object of converting it to trichloroethylene.

Sponsored Projects

Work on isolation of Ferberine from berberis bark has been completed during the period. Work on 12 sponsored schemes from the previous period was continued, while 4 new sponsored schemes have been started. Work on water evaporation control project was continued and 10 kilo of the fatty alcohol mixture has been prepared from cotton seed oil. Fabrication of electron diffraction equipments has been undertaken for

three parties. In a new sponsored scheme, design and fabrication of a plant producing 10 kg. of $TiCl_4$ /hr. has been undertaken. Vaporisation of refractory sulphides such as La_2S_3 , Ce_2S_3 and MnS , has been attempted. Preparation of acriflavine on laboratory scale has been concluded. Work on fractionation of hard resin of lac was continued. In the scheme on Tung oil, catalytic activity of various types of substances for the cyclization of the methyl. α - and β -eleostearates has been investigated. Action of sulphur as a cyclization promotor in the case of the trieneconjugated methyl eleostearate has been established for the first time. New crystalline compounds have been obtained from the following Indian medicinal plants: Punarnava, Shatavari and Putikaranja. A party producing pine oil from Indian turpentine oil, has sponsored a new scheme for standardization of the product. Costus roots from Punjab grown under various manurial and irrigational conditions, have been comparatively examined for yield of oil and lactones. A party producing l-menthol from dementholised peppermint oil has sponsored a project to simplify operations and improve yields in their existing process. A pilot plant of 1 kg./batch for the preparation of pharmaceutical grade calcium hypophosphite has been set up.

Research Projects and Schemes

Theoretical investigations were continued to elucidate the basic mechanisms which control the physical properties of solids and other molecular substances. Accordingly calculation of the thermal conductivity of ferrimagnetic solids has been completed. A combination of s-d mixing and s-d exchange has been taken into account to formulate a generalised Heisenberg type exchange interaction applicable to alloys having paramagnetic atoms \nearrow separated from each other. The impurities of the

produce localized states below and above Fermi surfaces. A new interaction mechanism involving these empty states above the Fermi surface has been formulated. The importance of vibronic interaction in giving rise to the unstability of certain modes has been fully explained. The work for the mobility in case of solid solutions of polar semiconductors has been completed.

Process for the preparation of permanent magnetic materials of magnetoplumbite structure with $(B \times F)_{max}$ of $1.7 - 1.8 \times 10^6$ gauss oersted is now ready for commercial exploitation. Needle-like single crystals of zinc oxide have been obtained. Studies on the crystallographic and electrical properties of $FeCuMnO_4$, $CuCrMnO_4$ and $NiMnCrO_4$ have been continued. The experimental results support the conclusion that Mn^{4+} and Cu^{1+} ions coexist in copper manganese spinels. During the trials for the production of semiconductor grade silicon from silicon tetrachloride, it has been found that the deposition takes place on a substrate maintained at $1100-1200^\circ$ by induction heating. Semiconductors of the compositions corresponding to $Bi_{22}Pb_{0.78}Te_{4.02}$ has a cubic structure and has shown good thermoelectric properties. New europium mixed ligand complexes containing β -diketone have been prepared as potential laser materials. Saw toothed wave generators developed previously in the laboratory for spreading the diffraction spots into rectangular or square areas were used for measuring the intensity of single crystal electron diffraction patterns of thin films of PbS and $PbSe$. Under controlled conditions, a basic nickel carbonate with low temperature of reduction and giving products of high surface area has been prepared. It was also found that the copper nickel catalysts containing 20-38% copper are substantially more active than the readymade imported catalyst

In the reaction between titanium tetrachloride and dimethyl sulphate a reactive monochloro intermediate of the composition $\text{ClTi}(\text{SO}_4)(\text{CH}_3\text{SO}_4)$ was obtained as a yellow powder. This compound reacts easily with hydroxylic organic compounds to give stable chlorine free organoxy-titanium compounds. Copper chelate of acetoacetiethylamide was prepared for the first time. In collaboration with RRL, Hyderabad, a process for obtaining nickel formate of catalyst grade has been successfully worked out. A new method for analysing microgram levels of vanadium using ferron has been developed. The silicofluoride of tetrazotised benzidine was prepared in about 80% yield. A $-\text{CF}_3$ substituted cupferron has been made starting from benzotrifluoride.

The resin from Ailanthus malbarica has been found to be a complex mixture of triterpenes. Acidic components of the gum Boswellia serrata have been found to consist of mainly 3-Boswellic acid, its acetate and the 11-oxo-derivative. In a non-volatile portion of the extract of Cedrela toona a new degraded triterpene similar to cedrelone has been isolated. The biologically active fraction of Hamycin is found to be similar to trichomyacin. A modified method has been developed for the preparation of CMC from moist ground-nut shell pulp. Hispidulin (dinatin) has been synthesized from 2,4,6-trihydroxy-5-methoxyacetophenone. It has been shown that gambogic acid corresponds to morellic acid and acetyl gambogic acid to isomorellic acid. A convenient method for the preparation of α -ar-turmerone from turmerone has been developed. α -Curcumene, which is free from isopropenyl isomer has been synthesized by two different routes. Isopatchoulene has been isolated from essential oil of cyperus cariosus.

Isopatchoulene has also been prepared from cyperene. By application of Wittig's reaction, tricycloekasantalic acid has been converted into optically pure α -santalene, α -santallic acid and α -santalol. Both the optically active forms of isobicycloekasantalic acid have been synthesized.

By condensing cyanuric chloride with hydrazine and interaction of the products with ethyl acetoacetate or ethyl benzoylacetate dye intermediates containing pyrazolone units have been prepared.

Preparation of diethylaminoethyl cellulose of required degree of substitution was developed.

The culture collection of NCIM now consists about 1200 non-pathogenic yeasts, bacteria and fungi. During the period 355 cultures were distributed to industrial concerns and research institutions. The presence of ubiquinone in S. griseus has been found; no ubiquinone is detected in A. niger whereas there is a rapid increase in the ubiquinone content on germination and in submerged conditions. A new method has been worked out for the preparation of soluble acetylcholinesterase from ox brain. Brain DP Nase has been obtained for the first time in soluble form from beef brain. Nitrite reductase which is 20 times more active than any other preparation reported so far has been obtained. Structure and stereochemistry of six products derived from limonene by fermentation with pseudomonad have been established by their chemical synthesis. A camphene-strain has been isolated by enrichment culture techniques. It has been established that this strain converts camphene to isoborneol by a prototropic rearrangement.

In the kinetic studies, polymerization of styrene with different Ziegler type catalyst systems such as $\text{ZrCl}_4-\text{AlEt}_3$

phthaloyl dibenzoyl peroxide is an effective catalyst for the telomerisation of ethylene with carbon tetrachloride. In the studies of polymerization of Indian turpentine oil, a low molecular weight solid has been obtained; similarly a resinous polymer has been obtained from Δ^3 carene. A modified styrene DVB base cation exchange resin has been developed by using different solvents as diluents and with improved techniques for washing the sulphonated copolymer. Samples of improved resin have been sent to few parties for evaluation. 1 kilo of the granular carboxylic cation exchanger from cold extracted CNSL has been prepared. Two sand filter saabs have been prepared and sent to Bombay Corporation for trials.

It is found that incorporation of proteins in rubber improves its physical properties. Tensile strength and modulus increase by about three times over that of pale rubber. The antioxidant obtained by condensing tetrahydroanacardol and sulphur monochloride is found to be comparable to similar imported antioxidants.

Production of acetanilide has been worked out on 20 kg/batch and a consistent yield of 97% acetanilide (99.6% purity) based on aniline used has been obtained. Complete chemical engineering data on the process has been passed on to a project engineering firm who have submitted a tender to HOC for a plant of 2000 tons a year.

Bench scale investigations to produce dibutyl phthalate in a 20-litre all glass distillation unit have been carried out. Several pilot plant runs have been carried out on 15 kg/batch scale for the production of dioctylphthalate. Necessary help was given to HAL, Pimpri in carrying out large scale pilot plant trials on vitamin C. Process design work on

hexachloroethane, dimethylaniline, acetanilide and phthalates and opium projects has been undertaken.

A new theoretical equation has been developed for estimating the diffusivity of a substance in a liquid starting from Eyring's diffusion equation. Kinetic studies on dehydration of ethanol over Indian bauxite have been completed. Work on the effect of pulsation and hold up on flooding in mass transfer has been completed.

ORGANIZATIONAL SET UP (as on 30th September 1965)

DIRECTOR
 JOINT DIRECTOR
 DEPUTY DIRECTOR

AUXILIARY TECHNICAL

DIVISIONS

ADMINISTRATION
 Man. Officer
 Accounts Officer
 Section Officers (4)
 I, II, III and
 Purchase Officer
 Medical Unit
 Maintenance & Security staff
 Civil Engineering staff

Sanctioned strength (Regular + pilot plants)

	PHYSICAL CHEM.	INORGANIC CHEMISTRY	ORGANIC CHEM.	ESSENTIAL OILS	BIOCHEM.	POLYMER CHEM.	CHEM. ENGG.	O. I. D.	DTS	FINE CHEM. SER.	ENGG. SER.
E	3	1	1	1	1	1	1	1	1	1	1
C	5	2	4	-	3	1	3	2	-	-	-
B	13	6	7	7	7	4	11+2	2	2	2	1
A	1	1+1	6	2	1	4	5+1	1	1	-	-
.A.	13	11+1	17	10	15	12	8+2	2+4	5	8	-
.A.	20	10+1	7	10	2	4	3+5	2+1	2	8	-
.Tech.	17	7	16	6	10	7	5+1	6+9	8	13	62

RESEARCH STAFF: DIVISION-WISE AND CATEGORY-WISE (as on 30th September 1965)

Working staff

Category	Physical chem.	Inorganic Chemistry	Organic Chem.	Essential oils	Biochem.	Polymer Chem.	Chem. Engg.	O.I.D.	Fine Chem.	D.T.S.	Engg. Ser.
	3	1	1	1	1	1	1	1	1	1	1
	3	2	4	-	2	1	2	-	-	-	1
	13	6	7	7	7	4	8+1	2	1	2	1 (STO)
	1	1	4	1	-	3	3+1	1	-	1	-
	12	11+1	16	10	15	10	6+2	2+3	8	4	-
	18	9	6	9	2	4	3+3	2+1	6	2	-
tech.	15	7	16	6	8	7	5+1	6+5	12	8	58
Officer	2	2	1	-	2	-	-	-	1	-	-
	3	-	1	2	1	-	-	-	-	-	-
	19	12	29	18	8	3	1	5	-	-	-

2. PILOT PLANTS

1. Fine Chemicals (1964) (Dr. P.K. Bhattacharyya)

The aim of the Fine Chemicals Project is to make available research chemicals that are so badly needed by scientific workers throughout the country and which are unavailable at short notice. Further, the chemicals prepared by the F.C.P. are almost entirely imported from abroad and hence their production at NCL would result in the saving of much needed foreign exchange.

During the past half year, the activities of the FCP have been stepped up. A process for the manufacture of phenoxy acetic acid on a large scale has been developed and the present production capacity of 25 kg./batch is now being expanded to accommodate the entire demand of the nation. (about 18 tons annually).

The pilot plant for production of malonic acid at 10 kg/batch has been set up. A method for the laboratory scale preparation of sorbic acid from by-product malonic acid has been standardized. During the half year, some 200 chemicals are being routinely manufactured. The following is a statement of orders executed during the half year.

<u>Period</u>	<u>Value of orders executed</u>
1st April 1964 to 31st March 1965	Rs. 31,470.97
1st April 1965 to 30th September 1965	Rs. 26,765.00

2. Dissolving pulp project (1958) (Mr. D.S. Bendale)

Investigation of indigenous cellulosic raw materials for dissolving pulp production.

Prehydrolysis sulphate pulping of *D.strictus* and *B.arundinecea*, species gave pulps of acceptable reactivity and chemical composition. Acid prehydrolysis sulphate pulp viscose solutions when spun gave rayon filament yarn of good physical properties. The yield of bleached pulps by above processes was not satisfactory. A two-stage alkaline pulping process was developed. This process is based

on removal of pentosans by alkaline liquors at high temperature and gives pulps of 90 to 97 per cent α -cellulose with less than 5 per cent pentosan content. Pulps are reactive and yield viscose solutions of acceptable filterability, filament yarn of proper tensile strength and elongation. The time of pulping is less and bleached pulp yield is comparatively more than prehydrolysis sulphate process. These findings were confirmed on pilot plant scale with recycling of black liquor. Except slightly higher iron content all other properties of these pulps fall in the reported literature range. Groundnut shells were investigated by different pulping methods and pulps were tested for carboxy methyl cellulose preparation. Depithed bagasse gave better pulp by water-prehydrolysis soda process.

Pilot plant trials on groundnut shells by water prehydrolysis-sulphate process have given unbleached pulp yield of 30 to 32% with 3 per cent pentosan and 4.4 cp. viscosity. On multistage bleaching, bleached pulps has following chemical analysis.

α -cellulose, 88-90 percent, pentosan 2.2 to 2.7 per cent. Degree of polymerization 550-510. Ash - 0.24 to .4 per cent. As these pulps could not be converted to sheet form due to small fiber length, processing of above pulps is carried out in wet conditions by suitable modifications in carboxymethyl cellulose process.

Groundnut shell pulp CMC falls in medium and low viscosity range with 0.5 to 0.6 degree of substitution. 1.7 kg. pulp is sent for testing its suitability to H. Kohnstamm & Co. Inc., USA.

As desired by the Director of Industries, Tripura State, work on Melocanna-bamboo species has been undertaken. Comparative study by different processes confirmed that acid prehydrolysis sulphate and two-stage alkali pulping processes are suitable for this species. As per suggestions of cellulose Adhoc committee further work on this species has been continued. By use of temperature between 130 to

Na_2O and 170° temperature with 25 to 30 per cent Na_2O in 2nd stage of pulping for 10 to 30 minutes results in pulps of less than 5 per cent pentosan.

Few experiments have been carried out with mix hard woods and first year growth bamboo from Maharashtra State as per request of Forest Utilization Officer, M.S. Prehydrolysis-sulphate process gives pulps of good chemical composition with high ash content. Further work is necessary for detail study.

- 1) Continuation of work on bamboo as per recommendations of cellulose Adhoc Committee by T.S. alkali process and study of hardwoods under optimum conditions of bamboo.
 - 2) Investigation of eucalyptus hybrid for type-cord and cellulose-acetate grade pulps.
 - 3) Purification of pulps - study of complex forming agents like diethyl triamine penta-acetic acid and n-hydroxy ethyl ethylene diamine triacetic acid.
3. Chlorination of titanium bearing (and other) materials and production of rutile titania pigment (1961)
(Dr. V.V. Dadape)

To utilize Indian ilmenite for the preparation of titanium tetrachloride and its subsequent hydrolysis to produce rutile titania pigment.

Upgraded ilmenite ore (90% TiO_2 content) has been chlorinated in 4" and 6" dia. refractory tube reactors and an optimum rate of 1 kg. of titanium tetrachloride per hour in an eight hour run was achieved.

Titanium tetrachloride thus obtained is hydrolysed at 60° and the titanium hydroxide after suitable washing is ignited to about 1000° to obtain pigment grade rutile titania. The operation of hydrolysis is carried out on 1 kg. scale.

The above scheme will be terminated after 31st

4. Aniline (1963) (Dr. L.K. Doraiswamy)

To design and operate a pilot plant for the vapour phase hydrogenation of nitrobenzene to aniline and *o*-nitrotoluene to *o*-toluidine.

The pilot plant (about 7 kg. per hour) set up earlier is operated and is found to give 80-85% conversion to aniline. Subsequently, on the advice of the Process Development Panel it has been decided to set up another reactor of the multi-tubular type. This reactor which employs hot oil as heat transfer medium has been set up and preliminary runs have been carried out.

Continuous runs are in progress on the life of the catalyst in a small glass reactor. It has been found that the catalyst even after over 800 hours of use is as active as at the beginning.

Engineering data will be collected on the new pilot plant, and this plant run continuously to assess the life of the catalyst on a larger scale. The work will be extended to *o*-toluidine.

It is expected that the project will be completed in March 1967.

5. Dimethylaniline (1963) (Dr. L.K. Doraiswamy)

To obtain chemical engineering data for the design of a commercial plant for dimethylaniline.

The continuous pilot plant is run for durations varying from 6 to 36 hours. Yields of the order of 90% based on aniline have been obtained. However, the final product is not free from monomethylaniline, and also the loss of methanol as dimethyl ether is quite substantial. Further work on the continuous process is stopped since it is felt that in view of the requirement of dimethylaniline for defence and other purposes a batch process can be quickly developed.

Several runs have been carried out in one litre autoclave and the process conditions finalised to obtain dimethylaniline (of over 99.6% purity) in a yield of 95%. The yield based on methanol is of the order of 85-90%. Arrangements have been made to carry out the reaction in a 30-litre autoclave. This autoclave will produce 8-10 kg. of dimethylaniline per batch. After completing work on this autoclave, a plant of about 600 tons per year capacity will be designed.

The continuous pilot plant set up for dimethylaniline will be used for the production of monoethylaniline from ethanol and aniline. It is believed that the continuous plant will work far more satisfactorily for this compound than for dimethylaniline.

It is expected that the project will be completed by March 1966.

6. BON Acid (1961) (Dr. L.K. Doraiswamy)

To develop a process for BON acid and to extend to the salicylic acid.

There is no progress on this project since the entire staff of this project is assigned to several other important schemes of this laboratory. However, a few runs are carried out to extend the method developed for BON acid to salicylic acid.

This project will be completed in March 1966.

7. Chlorination of Ethylene (1963) (Dr. L.K. Doraiswamy)

To develop a process for the production of hexachloroethane, trichloroethylene and tetrachloroethane.

A process for hexachloroethane has been developed. This process has been handed over to a firm in Gujarat and the complete chemical engineering design for a plant of 500

Work is also in progress to optimise the conditions for the production of tetrachloroethane from ethylene and chlorine with the object of converting it subsequently to trichloroethylene. Direct conversion of ethylene to trichloroethylene is also being investigated.

It is expected that this project will be completed in March 1967.

Work on this project could not progress to a significant extent during this period since the entire staff of this project was assigned to several other important schemes.

3. SPONSORED PROJECTS

1. Work on Investigations of the Synthesis and Properties of New Type Glycol Monoalkyl Ethers for the Control of Water Evaporation to Extend the Industrial Utilisation of Cotton Seed Oil Under PL-480 (U.S. Department of Agriculture, Washington (1964) (ABB)

Work is divided into two aspects: (1) preparation of cetostearyl alcohol mixtures by the hydrogenolysis of cotton seed oil, and (2) collection of basic data on monolayer properties of long-chain alcohols including alcohol mixtures obtained from cotton seed oil and alkoxy ethanols.

Preparation of cetostearyl alcohol

Using the method reported earlier, 10 kg of the alcohol mixtures from cotton seed oil have been prepared. The water evaporation retardation of the cetostearyl mixtures have been studied under semi-field conditions. Cetostearyl alcohol films, both synthetic as well as natural, show better water evaporation reduction and durability than the cetyl alcohol films.

Surface viscosity measurements

Surface viscosity measurements of n-long chain alcohols (C_{16} , C_{18} , C_{20} and C_{22}) at different shear rates and pressures have been done at 25° using a rotational viscometer. The results are used to calculate the change in free activation energy for viscous flow, intermolecular interaction, and relaxation time in various two dimensional phase changes of monomolecular film.

Thermodynamic properties of aqueous solutions

The density, refractive index and surface tension of aqueous solutions of the lower homologues such as methyl, ethyl and butyl cellosolves have been determined at different concentrations and temperatures for calculating their surface thermodynamical properties. Preparation of propyl cellosolve and carbitols is under progress.

Specific resistance to evaporation

used to study the monolayer properties of $C_{16}\text{-OH}$, $C_{18}\text{-OH}$, $C_{18}\text{-(OCH}_2\text{CH}_2)_2\text{OH}$, $C_{18}\text{-(OC}_2\text{H}_4)_3\text{OH}$ and $C_{22}\text{-(OC}_2\text{H}_4)_2\text{OH}$ at room temperature and various pressures. The specific resistance values are found in agreement with earlier results. Similar measurements at higher pressures and temperatures are under progress. The specific resistance values for $C_{18}\text{-(OC}_2\text{H}_4)_2\text{OH}$ and $C_{18}\text{-(OC}_2\text{H}_4)_3\text{OH}$ are comparatively lower than those for $C_{22}\text{-(OC}_2\text{H}_4)_2\text{OH}$. This result confirms that the former compounds form expanded film whereas the latter condensed one. This is in accordance with the previous observation on the pressure-area isotherm measurements.

2. Fabrication of electron diffraction equipment (1965)
(Dr. A. Goswami)

The work on fabrication of cameras, one for Gauhati University and one for Fertiliser Corporation, Sindri has already been undertaken and one of the equipments is in the process of completion.

3. Production of titanium tetrachloride from ilmenite
(M/s Travancore Titanium Products Ltd., Trivandrum.)
(1965) (Dr. V.V. Dadape)

The sample of titanium tetrachloride produced by our pilot plant process was found satisfactory by M/s Travancore Titanium Products Ltd., Trivandrum (Kerala) for the preparation of rutile titania seed material needed in their titanium dioxide plant. They have now sponsored the following scheme.

The problems to be undertaken are : (1) A bench scale unit (capacity 2 kg. TiCl_4 per hour) to be set up and worked during the first six months of the scheme.
(2) The data obtained on the bench-scale experiments will be utilized to set up at Trivandrum a pilot plant unit for the production of titanium tetrachloride (10 kg/hour to be gradually increased to 20 kg/hour).

The small unit producing 2 kg/ TiCl_4 per hour has been set up and run successfully.

The Travancore Titanium Products Ltd. have already deputed four research officers to the NCL for getting them acquainted and trained with the work of the NCL process.

4. Chemical and Thermodynamic Properties of Refractory Materials at High Temperatures - Under PL-480 (National Bureau of Standards, Washington (1964) (Dr. V.V. Dadape)

To investigate high temperature vaporisation of refractory oxides, sulphides, nitrides, etc.

High temperature vaporisations of La_2S_3 and Ce_2S_3 (prepared by reacting the respective oxides with carbon disulphide vapour at 900°) are attempted in the range of 1000° to 1200° employing transpiration technique. These sulphides have extremely low vapour pressures in the above temperature range, which is indicated by negligible weight losses in the system. The sulphides are highly susceptible to oxygen and are converted into oxysulphides, even if the carrier gas contains 1 ppm of oxygen. Precautions have been taken to employ highly purified carrier gas (Argon) in the above experiments. Similar technique has been used to study the vaporisation of manganese sulphide (MnS) at about 900° . This system also has very low vapour pressures at these temperatures ($800\text{-}900^\circ$). It is proposed to carry out the above work at still higher temperatures i.e. 1300° and above for rare earth salts and 1000 to 1500° for manganese salt.

5. Acriflavine (M/s Bhaidas Karsandas & Co., Bombay)
(1964) (Dr. Sukh Dev)

Starting from m-phenylene diamine, experimental conditions for the preparation of proflavine and its subsequent conversion to acriflavine have been worked out on a laboratory scale. The number of steps in the synthesis have been reduced to three by using a selective solvent

6. Constitution of Lac (Lac Research Institute, Ranchi)
(1961) (Dr. Sukh Dev)

The acid composition of the hydrolysed lac resin has been established almost quantitatively. It is concluded that the lac resin is a polymer derived from aleuritic and jalaric acid.

Work on the fractionation of hard resin is continued. By solvent precipitation and monitoring by TLC, a more or less homogeneous (functionality-wise) fraction has been obtained. Prolonged base hydrolysis of the fraction yielded only aleuritic acid and shellolic and lakhsholic acids, confirming thereby our previous conclusions about the nature of the building blocks of the lac resin.

7. Lac Dye (Indian Lac Cess Committee, Ranchi) (1957)
(Dr. K. Venkataraman)

Erythrolaccin : The synthesis of erythrolaccin, the structure of which has now been shown to be 1,2,5,7-tetrahydroxy-4-methylanthraquinone (Tetrahedron Letters 1963, 337), by an unambiguous method is nearing completion.

Laccaic acids : Part of the results so far obtained has been published in Bulletin of the National Institute of Sciences of India (1965, 28, 114). Work now in progress is mainly being concentrated on the chromatographic separation of the parent phenolic pigments. Two procedures which have shown some promise are preparative layer chromatography on silica gel impregnated with oxalic acid and column chromatography on polycaprolactam powder. It is hoped to describe some of the results obtained so far in detail shortly in one or two papers in the Indian Journal of Chemistry. The laccaic acid containing nitrogen and the acid which ultimately led to 1,3,6,4'-tetramethoxy-3'- ω -methoxyethyl-2-phenylanthraquinone obtained by a series of degradations and methylations are two constituents of lac dye which we hope to isolate as pure

The complete elucidation of their structures now appears to be a reasonable possibility.

In connection with the NMR spectra of the nitrogen-containing laccaic acid, several model compounds such as some derivatives of 8-hydroxyethyl-anthranilic acid are being synthesized.

The action of BF_3 -etherate and acetic anhydride on methoxyanthraquinones is being studied in detail. It has proved to be a useful reaction in examining the structures of ether-esters from the laccaic acids. Another reaction of interest in this connection which is also under study is the Marschalk reaction on purpurine-2-methyl ether using formaldehyde and alkaline dithionite, which yields 2,3-dimethylquinizarin as a result of the replacement of the methoxyl by a methyl group.

8. Reactive Dyes (Amar Dye Chem Ltd., Bombay) (1963)
(Dr. K. Venkataraman)

Work on this project has been continued and several new dyes have been sent to the firm for evaluation.

9. 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 under PL-480
(U.S. Department of Agriculture, Washington) (1963)
(Dr. Sukh Dev)

The work on tung oil aims at the development of new industrial chemicals - chiefly the cyclic monomer and dimer-resulting from the heat treatment of the oil.

The catalytic activity of a variety of types of substances (viz. sulphur, selenium, iodine, alkali, benzoyl peroxide, amberlyst resin, palladium, oxygen, vanadium pentoxides, selenium dioxide, cupric acetate and silic acid) for the cyclization of the methyl α - and

promoter in the case of the trieneconjugated methyl eleostearates has been established for the first time. Thus mild thermal-treatment (160° for 5 hr) of methyl eleostearate in the presence of a trace amount (0.2%) of sulphur resulted in a 25% conversion to the cyclic monomer (in the absence of the catalyst there was practically no cyclization under the same conditions); the dimer was formed to the tune of 10%. The regenerated ester from the urea-adduct is recycled to yield the cyclized material again in comparable yield. The cyclic monomer and the dimer have been chromatographically (GLC and TLC) investigated and isolation of chemically pure compounds from the mixtures is under way.

10. Composite Drug Research Scheme on Indian Medicinal Plants
(Ministry of Health, Govt. of India) (1965)
(Dr. Sukh Dev)

Work on the following three plants has been started.

- 1) Punarnava Boerhavia diffusa Linn.
(Nyctaginaceae)
- 2) Shatavari Asparagus Racemosus Willd
(Liliaceae)
- 3) Putikaranja Caesalpinia bounducella Flem
(Leguminosae)

Punarnava - Air-dried powdered roots have been subjected to successive extraction with Petroleum ether, Benzene, Chloroform, Ethyl acetate and Ethanol. Thin layer chromatography of these extracts shows them to be complex mixtures. One crystalline compound m.p. $136-7^{\circ}$ isolated from petroleum ether extract has been identified as β -sitosterol. Work on other extracts is in progress.

Shatavari - Dried roots have been extracted by n-Hexane, Ether, Ethyl acetate and Ethanol in sequence. From n-Hexane extract a crystalline compound m.p. $153-56^{\circ}$ has been isolated. It is most probably

Two crystalline compounds have also been obtained from ether extract. The ethyl acetate extract and ethanol extract consist mostly glycosides and carbohydrates.

Putikaranja - The powdered kernels of the mature seeds have been extracted successively with Pet. ether, Benzene, Chloroform, Ethyl acetate and Abs. ethanol. Thin layer chromatography of these extracts shows presence of a number of closely related compounds. Benzene and chloroform extracts are found to be quite similar. A small amount of a pure crystalline compound (m.p. $241-43^{\circ}$) has been obtained, which is found different from the previously reported α , β and γ -caesalpins.

Different extracts from all the above materials have been sent for pharmacological tests. Efforts will be made to isolate more amounts of pure compounds for systematic investigation.

11. Pine oil from Indian turpentine oil
(M/s Prabhat General Agency, Bombay) (1965)
(Dr. Sukh Dev)

To find out different constituents present in the pine oil and their characterization, and to improve the percentage of alcoholic portion.

Commercial Oil sample received from the party has been fractionated and GLC of different fractions has been recorded. The major portion of the oil has been characterized as Δ^3 -carene. Presence of p-cymene has also been confirmed. Work is in progress.

12. Research on Commercial Uses of Punjab Costus(Kuth) Roots
(Govt. of Punjab) (1963) (Dr. S.C.Bhattacharyya)

To find out ways for profitable utilisation of a portion of the costus roots grown in Lahaul and Spiti areas of Punjab.

A large number of samples of roots grown under various manual and irrigational trials supplied by the Government

Some more derivatives of dehydrocostus lactone and costunalide have been prepared and sent for pharmacological testing.

13. Improvements in the process for the manufacture of l-menthol from dementholised peppermint oil.
(M/s Bhavana Chemicals Ltd., Baroda) (1965)
(Dr. S.C. Bhattacharyya)

A leading producer of l-menthol in the country uses imported dementholised peppermint oil as the raw material. The process used by them is complicated and requires simplification. The party has sponsored a project in this connection.

The dementholised peppermint oil supplied by the party has been examined by separating it into various fractions by column chromatography and analysing each fraction by GLC. The results indicate that the dementholised peppermint oil can theoretically yield 68% l-menthol from l-menthol and l-menthone present in the oil.

The hydrocarbon fraction contains mainly l-limonene, β -pinene (traces) and Δ^3 -carene.

Some 20 fractions obtained during the distillation of dementholised peppermint oil from the M/s Bhavana Chemicals have been analysed by GLC and the results communicated to the party.

Work on the simplification of the process of isolation of menthol is in progress.

14. Preparation of Certain Vat Dyestuffs (M/s Amar Dye Chem. Ltd., Bombay) (1962) (Mr. P.G. Phadatare)

The objective of this scheme is to optimise process conditions for the production of certain vat dyes. Golden yellow G.K. has been taken up for detailed study in the first instance.

Conditions have been optimised for the production

of a vat dye and a brief report of the work has been submitted to the sponsor. A detailed report is being written up on this project.

Work on this scheme will be completed in March 1966.

15. Diethylmetaaminophenol (M/s Sahyadri Dyestuff & Chemicals (P) Ltd., Poona) (1965) (Dr. L.K.Doraiswamy)

To work out a process for the manufacture of the intermediate diethyl meta amino phenol, required for the production of certain basic dyes.

Conditions have been optimised for the production of this intermediate and experimental work has been completed. A detailed report is being written up.

This scheme will be completed in March 1966.

16. Manufacture of calcium hypophosphite (M/s Chunilal Ootamchand & Co., Bombay) (1964) (Dr. M. Goswamy)

The object is to develop process know-how on laboratory and pilot plant scale for the manufacture of calcium hypophosphite. We shall be supplying to the sponsor complete plant designs for commercial production of 30 kg./day and help him in fabrication and setting up the plant.

Calcium hypophosphite is manufactured by the direct reaction of yellow phosphorous with lime. The reaction products are calcium hypophosphite in solution, insoluble calcium phosphite, gaseous mixture of phosphine and diphosphine and hydrogen.

Bench scale experiments were completed to optimise the conditions of reaction to obtain maximum yield of calcium hypophosphite.

Setting up of a pilot plant (1.0 kg/batch) has been completed. Recovery of phosphorus in the phosphine as phosphoric acid by burning it with fuel gas and absorption of combustion product with water is undertaken. A burner for phosphine gas is developed and continually modified so that about 3 litres/min. of phosphine can be burned with 2 litres/min. of burshane gas and 50 litres/min. of primary

phosphoric acid and concentration of the latter by recirculation.

Factors such as temperature of reaction, ratio of phosphorus to water etc. are also studied. At 75-85° and phosphorus to water ratio of 1 : 30 the yield of hypophosphite is similar to that obtained in the bench-scale experiments. The filtration is carried out in a porcelain nutsche filter and concentration of the solution in a steam heated open S.S. pan.

Now that phosphorus has been made available to us, further runs will be taken with 1 kg/batch of phosphorus, improving the yield, preparing material of adequate pharmaceutical purity etc. leading to the design of an industrial unit of 30 kg/day of the product.

4. RESEARCH PROJECTS
and
SCHEMES

PHYSICS AND CHEMISTRY OF SOLIDS

A) Theoretical ResearchSolid State and Molecular Physics (1957) (Dr.K.P. Sinha)

Theoretical investigations are undertaken to elucidate the basic mechanisms which control the physical properties of solids and other molecular substances. More specifically, these are concerned with the electrical, magnetic, thermal and optical properties of certain substances. Fruitful ideas are applied for the development of materials and devices having suitable physical properties.

1. Phonon-magnon interactions in magnetically ordered solids (1961)

Atomistic theory of the interaction processes involving phonons and magnons in ferro-, antiferro and ferrimagnetic crystals was developed. The mechanisms of energy exchange between spin and lattice systems were clearly delineated and they were in agreement with observed results for the three types of magnetic crystals.

Based on the above studies, the calculation of the thermal conductivity of ferrimagnetic solids has been completed. The different scattering processes which were found to be important for the thermal conductivity in the low temperature regions are the phonon scattering by magnons, by mass defects and strain fields and boundary scattering. The total relaxation frequency ($1/\tau$) and thermal conductivity (K) are given by

$$\frac{1}{\tau} = A + Q \bar{\nu}^3 + P \bar{\nu}^4$$

$$K = \frac{k_B^4 T^3}{2\pi h^3 c} \int_0^{\theta_D/T} \frac{\bar{\nu}^4}{A + Q \bar{\nu}^3 + P \bar{\nu}^4} \frac{e^{\bar{\nu}}}{(e^{\bar{\nu}} - 1)^2} d\bar{\nu}$$

where $\bar{\nu}$ involves phonon wave-vectors. The integral has been evaluated graphically for ferrites ($MnFe_2O_4$) and garnets ($Y_3Fe_2Fe_3O_{12}$). The calculated results are in close agreement with the low temperature experimental data on these systems.

2. Interactions involving conduction electrons in magnetic metals and alloys (1963)

The role of s-d mixing (both intra-atomic and inter-atomic) was utilized to give a general interaction mechanism between magnons and conduction electrons in some metals and alloys. This gave processes of the type A ($S_{cx}S_{dx} + S_{cy}S_{dy}$), which were found to be of importance in giving rise to temperature independent relaxation processes.

A combination of s-d mixing and s-d exchange has been taken into account to formulate a generalised Heisenberg type exchange interaction which is applicable to some alloys where paramagnetic atoms are far separated from each other. It is found that the effective coupling has an oscillatory behaviour with distance. This mechanism has been applied to Hensper alloys e.g. Cu_2MnSb .

3. Super conductivity in metals and alloys (1963)

The problem of "pressure dependence of transition temperature in super conductors" was brought to a logical conclusion. The microscopic theory takes into account of the fact that owing to external pressure a modulation in the crystal and impurity potential is brought about. The resulting perturbation gives rise to interband and intraband transition of electrons. The theory predicts a decrease or an increase of the transition temperature as a function of the pressure dependence on the magnitude of certain matrix elements involved. This has explained a large body of experimental results.

The effect of the impurities of the transition elements incorporated in superconducting substances has been undertaken. The important point in this study is that the increase of transition temperature is associated with only those systems which do not show any net magnetic moment. However, the impurities produce localized states below and above the Fermi surfaces. A new interaction mechanism involving these empty states above the Fermi surface has been formulated. It is found that this effect leads to an additional attractive interaction between a pair of superconducting electrons.

The role of such processes in the increase of transition temperature will be investigated.

4. Vibronic interaction in ferro- and anti-ferro electric crystals (1963)

The role of Jahn-Teller effect for such systems was investigated and the collective oscillations in a system of linear ordered dipole was studied.

The importance of vibronic interaction (interaction of low lying electronic states with the ground state via the vibration of the complex-octahedral) in giving rise to the unstability of certain modes has been fully explained. It is shown that higher ordered anharmonic terms with vibration of the system can stabilize this and the temperature dependence of the frequency of the soft mode has the correct form. Further calculations in this direction will be continued.

5. Mobility in polar semiconductors (PbS, PbSe, PbTe etc.) (1963)

The formulation of a theory for the mobility in pure polar semiconductors was completed. This invoked the interband transition effects caused by optical phonons along with the scattering of the carriers by acoustic and other phonons. This resolved a long standing problem.

The work on the solid solutions of such systems has been completed. In addition to the temperature dependence the variation with respect to the concentration of one of the components (PbSe-PbTe) is also explained. One phonon scattering process for the carrier along with the modifications of the carrier state due to alloying perturbation gives

$$\mu = \mu_0^{(s)} T^{-3/2}$$

$$\text{where } \mu_0^s = \frac{c}{a \sum_{r,s} f_r f_s |f_r f_s|^2}$$

and depends upon the concentration f_r and f_s of the two components. This explains the observed temperature and concentration dependence for many systems.

Based on the carrier states stipulated in the above formulation, the behaviour of carriers in the presence of magnetic fields will be studied.

6. Electronic structure of molecules (1964)

The π electron systems and their densities in dibenzanthrene and its derivatives were studied on the basis of electron gas model.

These calculations have been extended to the following systems

(i) Benzene and benzoquinone, (ii) Anthracene and anthraquinone, and a few other molecules and their derivatives, particularly dyes. For treating the derivatives a δ function type potential $V_c \delta(r-r_1)$, where V_c is constant, has been introduced. The wave functions and energy eigen values have been calculated. This method seems to work fairly well.

The calculation of the density of π electrons is in progress. This type of work is to be extended to many more molecules.

7. State of atoms in the presence of crystal and radiation fields (1965)

This work has been initiated recently. The idea is to study the spin and electric states of paramagnetic atoms in crystal in the presence of the static and oscillating fields. After getting a knowledge of this, the interaction with radiation fields will be undertaken. The study is connected with the laser action of such materials.

8. Magnetic break-down in solids (1965)

This is a new field and has opened up new lines of research and application.

In this work the electron orbits (in K space) are determined by the inter-section of the surfaces of constant energy with planes normal to the magnetic field. If the electron trajectories thus derived belong very nearly to the same energy and also approach very closely in K space, the phenomenon of magnetic break-down occurs. The present approach is essentially based on the fact that there is a finite probability in the case of the near crossing of two paths that the adiabatic path is not followed. In these circumstances the probability for this event gives the criterion for the magnetic break-down. Taking into account the

presence of magnetic field the Schrodinger equation for the problem is set up. The solutions of this equation come out to be hyper geometric cylindrical functions.

It is proposed to obtain the probability that the adiabatic path is not followed by using the technique of analytical continuation.

B) Material Research

1. Ferromagnetic materials (1959) (Dr.A.P.B. Sinha)

New ferrites are being synthesized with a view to develop ferromagnetic materials suitable for high frequency applications.

Work on anisotropic permanent magnetic materials of magnetoplumbite structure is continued. By a proper choice of composition, preparation conditions and doping agents, it has been possible to get $(B \times H)_{\max}$ of $1.7 - 1.8 \times 10^6$ gauss oersted for unoriented samples. This process for making permanent magnets is now ready for commercial exploitation.

(Ni,Zn) and other isomorphous ferrites have been developed for medium and short wave applications. (Mg,Mn) ferrite suitable for microwave applications have been synthesized.

Some new ferromagnetic oxides isomorphous with perovskite have been synthesized and their structure and saturation magnetisation determined.

Attempts are being made to substitute fluorine partially for oxygen in the ferrites of spinel and magnetoplumbite structures with a view to improve the magnetic properties. Fluorine containing compounds under investigation are (i) lithium ferrite, and (ii) Cu, Mn, Co, Ni substituted ferrites of the composition $PbF_2 \cdot (6-x)Fe_2O_3 \cdot xMo$ or MF. The powder diffraction patterns and the saturation magnetisation values have been obtained.

2. Semiconductors (1958) (Dr.A.P.B. Sinha)

New type of oxidic semiconductors are being synthesized and their properties are being studied.

Needle-like single crystals of zinc oxide have been obtained by heating zinc sulphide powder at 1170° in a controlled atmosphere ($P_{O_2} \times 10^{-3}$ atmospheres). In the temperature range of $25-200^{\circ}$ they exhibit n-type conductivity with an activation energy of 0.02 ev. The charge carriers (electrons) arise due to the ionisation of neutral oxygen vacancies and neutral zinc interstitials. At $200-600^{\circ}$ the conductivity changes to p-type and activation energy becomes 0.92 ev. This change has been attributed to the ionisation of vacant zinc sites. The resistance decreases after annealing at 600° presumably due to the increase in the concentration of zinc and oxygen vacancies and zinc interstitials.

Absorption spectrum shows an absorption edge at $390 m\mu$ corresponding to a band gap of 3.24 ev.

These zinc oxide crystals have been irradiated by γ rays obtained from a Co^{60} source. Changes in the defect structure have been followed by measuring the electronic conductivity. The results indicate that absorbed oxygen reacts with oxygen vacancies and electrons taken from the dissociation of interstitial zinc.

Studies on the crystallographic and electrical properties of $FeCuMnO_4$, $CuCrMnO_4$ and $NiMnCrO_4$ have been continued. All the three compounds exhibit the cubic spinel structure. The cation distribution has been worked out from the analysis of x-ray diffraction intensities. Measurements of electrical conductivity as a function of temperature have been carried out. The experimental results support the conclusion that Mn^{4+} and Cu^{1+} ions coexist in copper-manganese spinels.

3. Silicon semiconductors (1959) (Dr.A.P.B. Sinha)

Preparation of semiconductor grade silicon is being tried.

A unit for the preparation of silicon tetrachloride from ferrosilicon has been run continuously. Purification of this silicon tetrachloride has been achieved to give a starting material of adequate purity. An apparatus for the epitaxial growth of silicon by the reduction of silicon tetrachloride vapour with pure hydrogen has been set up. The deposit of silicon takes place on a substrate maintained at $1100-1200^{\circ}$ by induction heating.

4. Electrical and thermal properties of semiconductors (1962) (D_r.K.P. Sinha)

On the basis of the theoretical concepts developed, the following experimental work was undertaken. It has been reported earlier that the apparatus for measuring the thermoelectric power (α) resistance (ρ) and thermal conductivity (K) was fabricated utilizing the Peltier effect. Results of the measurement on Bi_2Te_3 doped with magnetic impurities were reported.

Similar measurements on $PbTe$ doped with paramagnetic impurities have shown that the resistance increases with doping concentration initially, but falls down with higher concentration. The thermal conductivity on the other hand, decreases with an increase of concentration up to 0.16 atomic % on Mn and then rises. The thermoelectric power behaves in the same manner.

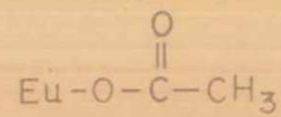
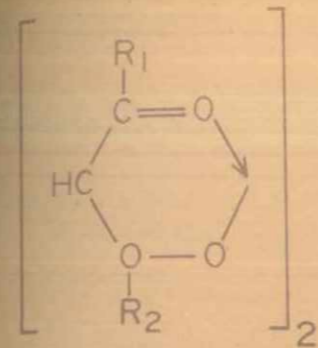
The work on the solid solutions Bi_2Te_3 and $PbTe$ has given some valuable results. A composition corresponding to $Bi_{2.2}Pb_{0.78}Te_{4.02}$ has a cubic structure and shows good thermoelectric properties. Other compositions are under study. It is proposed to extend the activity of this work by setting up an equipment for measuring magneto-thermal conductivity.

5. Laser materials (1964) (Dr.A.P.B. Sinha)

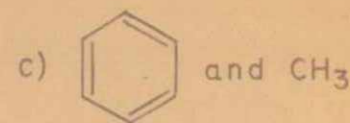
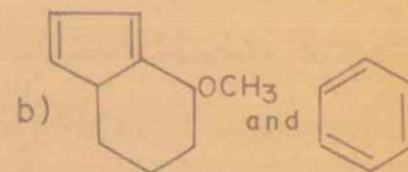
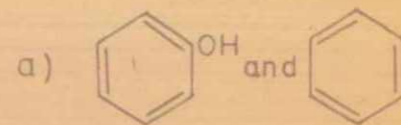
New europium mixed ligand complex are being prepared which are useful in lasers.

LASER MATERIALS

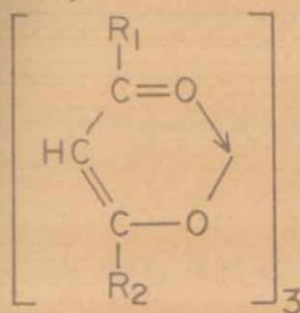
New europium chelates viz. (a) mixed ligand complexes containing β -diketones and the acetate ion.



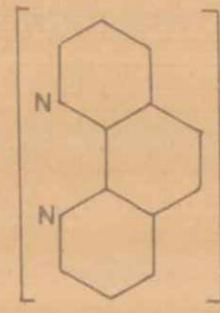
where R_1 and R_2 are

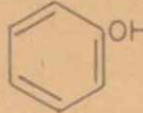



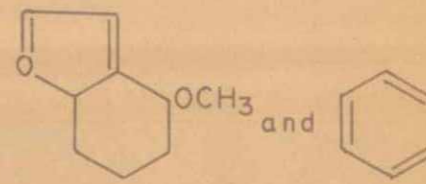
(b) β -diketonates complexed with nitrogen donors.

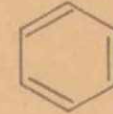


Eu

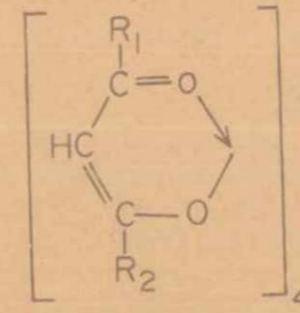


where R_1 & R_2 are  and ,



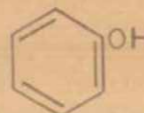
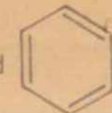
or  and CH_3 respectively;

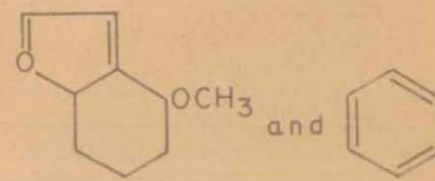
and (c) β -diketonates complexed with Lewis bases

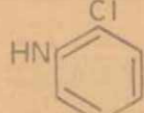


Eu HP

(P=piperidine or NH_2)

where R_1 & R_2 are  and ,



or CH_3 and  respectively;

Current voltage characteristics of metal-insulator-metal thin film sandwiches have been studied. Very thin films of insulator give tunneling characteristic while thicker films give space charge limited current flow. The effect of electrode has been studied in thicker films and it agrees with the space charge limited current flow. Thick insulating film diodes such as Al-Al₂O₃-Al; Au-Cds-Al show current controlled negative resistance characteristic while diodes in which organic metal chelates have been used as insulating material give voltage controlled negative resistance. Some of the organic insulators such as anthracene and Cu-phthalocyanene show space charge limited current flow. The effect of temperature is large on thicker insulating film diodes than that on thin insulating film diodes. The exact mechanism of negative resistance and effect of temperature and light on it is under study.

6. Photoconducting properties of semiconductors (1962)
(Dr. A. B. Biswas)

Photoconductivity of PbS films is under study with a view to collect mechanism of photoconductivity and eventual development of photoconductive devices.

The resistivity characteristics of PbS films prepared earlier have been investigated as a function of temperature down to -160°. The oxygen treatment by baking at temperatures up to 200° shows significant influence on activation energy. A few vacuum sealed photoconductive cells have been constructed. A high gain low-frequency amplifier detector has been constructed for studying the response of these cells to chopped radiation. CdSe photoconducting films have been prepared by vacuum deposition. The spectral response has been studied and the energy gap calculated. An apparatus for studying effect of oxygen and other ambients on the photoconducting properties of these films has been constructed.

7. Ferroelectric materials

Structural and dielectric studies
 (a) (1957) (Dr. A.B. Biswas)
 (b) (1964) Dr. P. Roy Chaudhary

The investigations are aimed at preparation of newer and potential ferroelectric materials and to study their structural and other characteristics in relation to their ferroelectric and allied properties, with a view to understand the basic principles involved, so that applications of their properties can be made.

a) Ferroelectric properties of the perovskite type titanates prepared earlier are investigated by measuring hysteresis loops, spontaneous and remanent polarisation, and coercive field, as a function of temperature. Dielectric properties of solid solution in the system $BaZrO_3 + (1-X) BaNb_2O_6$ have been completed at room temperature and various frequencies. Three compositions in the orthorhombic regions are studied in detail to find out the ferroelectric transitions, since the dielectric constant temperature data do not give information on this transition. Study of the hysteresis loops at various voltages is in progress.

A variable frequency oscillator (100 Kc-10 Mc) is under fabrication for the study of the piezoelectric coupling coefficient. The study of the effect of temperature on the spontaneous polarisation, remanent polarisation and coercive field of the various compositions in the system $Ba_xPb_{(1-x)y/2}Nb_yZr_{(1-y)}O_3$ is in progress.

b) Some of the ferroelectric compositions of the system $Pb(Fe_{\frac{1}{2}}V_{\frac{1}{2}})_xTi_{1-x}O_3$ are studied. It has been observed that if Fe^{3+} is replaced by La^{3+} , the compositions show better hysteresis loops and increased amount of spontaneous polarisation. The study of the sample $Pb(La_{\frac{1}{2}}V_{\frac{1}{2}})_{0.2}Ti_{0.8}O_3$ has been completed. As before, a modified Sawyer-Tower circuit has been used for the display of ferroelectric hysteresis loops on the cathode ray tube at 50 c.p.s. ac field. The loops are traced out for a series of field strength (Max. 30 KV/cm) at room temperature and corresponding spontaneous polarisation vs. field strength are

shows a sharp rise and then flattens up. By extrapolating the the flatten portion back to the polarisation axis, the permanent polarisation characteristics in zero field has been estimated for this sample, as 1.4 micro coul./cm². Curie temperature is determined from measurements made on at least for three samples of a particular composition prepared under optimum firing conditions. The slope at zero voltage of the hysteresis loop

$$\tan \alpha = \left[\frac{E_y}{E_x} \right]_{E=0}$$

is a measure of the initial dielectric constant of the ceramic under the conditions chosen. At room temperature, the initial dielectric constant, K is 850 which rises to 1400 at curie temperature. The dielectric constant as determined by a capacitance bridge at 10 KC/S and a Q-meter at 100 KC/S are 530 and 503 respectively. The curie temperature, as determined with these instruments is 90°. The study of other compositions of these series is being carried out.

C) Thin Films (Dr. A. Goswami)

In thin film states properties of materials are often different from the bulk and consequently thin films are finding wide and specialised applications. In view of the above, fundamental studies on the semiconducting, optical and other properties of thin films and their detailed structures have been undertaken.

1. Structure of thin film (1958)

Electron diffraction studies have been made on the vacuum deposited films of selenides and tellurides of zinc, cadmium and bismuth, crystal growth process, phase transformation with temperature. Selenides and tellurides of zinc and cadmium grow epitaxially on single crystal substrates at high temperature which favoured parallel orientations. At low temperature even though the first few layers in contact with the substrates are two-degree orientated, further continuation of the epitaxial growth is entirely dependent on other factors e.g. substrate temperature, rate of deposition and the lattice fit between the

phase and the appearance of $[211]$ and $[115]$ orientations are no doubt due to the stacking fault, causing extensive $[111]$ twinned structure. In the case of CdSe the deposits develop odd orientations viz. $[10\bar{1}1] + [20\bar{2}3]$ and $[20\bar{2}5]$ respectively on $[100]$ and $[110]$ face of rock-salt.

Bi_2Se_3 and Bi_2Te_3 develop a modified hexagonal structure equivalent to pseudo-cubic structures (Bi_2Se_3 , $a_0 = 3.06 \text{ \AA}$, and Bi_2Te_3 , $a_0 = 3.25 \text{ \AA}$). These deposits also grow epitaxially on the different faces of rock-salts. Bi_2Se_3 , however, on prolong heating decomposes to BiSe ($a_0 = 5.99 \text{ \AA}$) growing epitaxially on all (100), (110) and (111) faces of rock-salt with a strong tendency to develop facets.

Saw-tooth wave generators developed previously in the laboratory for spreading of the diffraction spots into rectangular or square areas are used for measuring the intensity of single crystal electron diffraction patterns of thin films of PbS and PbSe. This device is now being given a thorough trial for standardization.

2. Physics of thin films (1962)

A systematic study of semiconducting properties of thin films of varying thicknesses of several semiconductors is made and the measurements of semiconducting parameters for thin films are standardized for the first time. The effect of factors such as thickness, rate of evaporation, substrate temperature on parameters viz. resistivity, thermoelectric power, Hall coefficient, TCR, mean free path etc. are also studied. The size effect, imperfections, surface asperities, concentration of defects which controlled the thin film properties in the same way as impurities in the bulk are established. The above studies are also followed by the electron diffraction study of the surface structures.

Investigations on the Hall coefficient (R_H) of various film thicknesses ranging between

with respect to thickness, dimensional ratio (l/b) annealing and the substrate temperature. R_H is found to increase continuously with rise in thickness, unlike bulk material, but remained unaffected by current, field strength and also by l/b between 3:1 to 6:1. With annealing R_H dropped down and sometimes to 1/10 of its value as found in case of Sb_2Te_3 films. Increase in substrate temperature, however, raises the R_H value.

D) Structural Studies (Dr.A.B. Biswas)

1. Structural properties of semiconductors (1958)

Electrical conductivities of solid solutions of manganites CuMn_2O_4 (Cubic) + NiMn_2O_4 (Cubic spinel) and $\text{CuMn}_2\text{O}_4 + \text{MgMn}_2\text{O}_4$ (tetragonal spinel) have been measured in the temperature range 25-800° with a view to determine the temperature coefficient of resistances and the composition dependence of activation energy (ΔE).

2. Crystal and molecular studies (1959)

Crystal and molecular structures of selected compounds are being studied for correlation with their physical and chemical properties.

A theoretical study has been made of diffuse X-ray scattering from neutron irradiated graphite. The results agree with the experiments of Bacon & Warren (Acta Cryst. 1956, 9, 1029) on irradiated graphite samples. It is concluded from the theory that the displacement due to the interstitial atom, in graphite layers decreases at a slower rate with increasing distance (from the interstitial atom) than that given by the inverse square law.

The detailed refinement of the structure of p-Nitrobenzoic acid by three dimensional method has been completed. Bond lengths and bond angles have been measured with an accuracy of $\pm 0.01 \text{ \AA}$ and $\pm 0.5^\circ$ respectively. There is evidence of a slight distortion of the molecule from planarity.

The structure analysis of benzoyl glycine is in progress. Signs of about 20 hko structure factors are obtained by the method of inequalities and by using Sayre's equation. These signs along with observed magnitude of the structure factors are used to get the (001) Fourier map. Trial structures are now being set up on the basis of this map. The work is in progress.

Crystal and molecular structure of Ni-imidazole nitrate hydrate is also in progress. Relevant experimental data for copper-acetyl glycine have been collected. The crystal structure of O-nitrobenzoic acid has been refined by using two dimensional method. Refinements of the structures of sodium 2-oxo-valerate and sodium 2-oxo-heptylate are being done successively by the direct Fourier, Difference Fourier and Least Square methods.

3. Spectrochemical studies (1963)

Spectral characteristics of compounds are studied for correlation with their molecular structures and physicochemical properties.

Studies on the infrared spectra of long chain alkoxy ethanols were extended to the compounds $\text{CH}_3(\text{CH}_2)_{17}(\text{OCH}_2\text{CH}_2)_2\text{OH}$, $\text{CH}_3(\text{CH}_2)_{17}(\text{OCH}_2\text{CH}_2)_3\text{OH}$ and $\text{CH}_3(\text{CH}_2)_{21}(\text{OCH}_2\text{CH}_2)_2\text{OH}$. Odd chain alcohols containing 17 and 19 carbon atoms have been prepared. A low temperature cell has been constructed for studying the IR spectra at the liquid nitrogen temperature.

Infrared spectra of salicylaldoxime, its deuterated analogue, oximino acetyl salicylaldoxime, oximino benzoyl salicylaldoxime, salicyl aldoxime diacetate are investigated in solution, to establish the hydrogen bonding properties of the oximino and phenolic hydroxyl groups. Contrary to earlier reports, it has been found that O-H...N hydrogen bond is weaker than the corresponding O-H...O bond. Deuterated analogues of substituted ureas have been prepared and their infrared spectra analysed to assign the relevant bands.

The transition metal complexes of benzoyl and glycine

of $650-4000 \text{ cm}^{-1}$. The results are being reviewed in the light of metal sensitive bands. The transition metal complexes of ortho-, meta- and para-benzoic acids are prepared. The IR spectra of these acids are studied in the solid state and in dioxan. The results confirm the zwitterion structure for the meta amino benzoic acid in the solid state.

4. Magnetic susceptibility studies (1965)

The magnetic susceptibilities of Cu(II), Co(II), Ni(II) and Mn(II) complexes with lactic, malonic, mandelic and tartaric acids have been measured at room temperature on a Gouy Magnetic balance. All the metals are found to have an octahedral coordination. Paramagnetic susceptibility of transition metal complexes of maleic and fumaric acids have also been investigated.

Preliminary work has been started on the determination of magnetic susceptibilities of manganese tellurides and nickel oxide (containing varying proportions of copper oxide) over a wide temperature range.

E) Thermodynamic Properties of Solids (1958)

1. Low temperature calorimetry

Heat capacities of potassium copper trifluoride and potassium nickel trifluoride have been determined at various temperatures in the range $78-300^\circ\text{K}$. For the former compound a transition from the antiferromagnetic to paramagnetic state has been observed. Thermodynamic functions are evaluated in conjunction with Kelley's extrapolation procedure.

2. High temperature calorimetry

The construction and calibration of an adiabatic calorimeter working in the range $25-300^\circ$, is reported earlier. A series of pervoskites of the type $\text{AB}_2\text{B}_2\text{O}_3$ where A = Strontium, B = Tungsten or Molybdenum and B' = Cobalt or Nickel are prepared for study.

various thermodynamic functions. The compound undergoes a transition at 179° which may be attributed to a structural transformation from tetragonal to a cubic lattice. The heat transition and the entropy of transition have been calculated for the compound.

3. Thermodynamic properties of coordination compounds (1965) (Dr.H.B. Mathur)

To determine the thermodynamic properties associated with the interaction of transition metal ions with aminoacids and β -diketones.

The thermodynamic quantities ΔF , ΔH and ΔS have been determined for the interaction of divalent cations of the transition series metals, Mn, Fe, Co, Ni, Cu and Zn with the amino acids serine, threonine in aqueous solution. The experimental data show that (a) the enthalpy changes are negative and entropy changes are positive in all cases, (b) order of enthalpy change is in agreement with the Irving-William order of divalent complexes. The unusual higher value of ΔS for cupric complexes ~~xxx~~ is due to the Jahn-Teller distortions of the octahedral symmetry of the complexes.

4. Oxidation behaviour of metals and alloys (1959) (Dr.A.B. Biswas)

The oxidation of vacuum deposited films of lead and bismuth are studied in oxygen atmospheres at 30 mm of Hg pressures in the temperature range $200-300^{\circ}$. A quartz balance constructed earlier is used for these studies. The kinetics of oxidation for the lead film show a direct logarithmic behaviour and that the bismuth films exhibit a parabolic character.

5. High temperature solid-gas-reactions and diffusion in solid state (1960) (Dr.H.B. Mathur)

To obtain basic data on intermetallic diffusion and high temperature oxidation of metals and alloys with special emphasis on materials of interest to nuclear reactor technology.

Studies on high temperature oxidation kinetics of copper, lanthanum, gadolinium and silver-indium alloys have been completed by three different techniques (i) Gulbransen type vacuum microbalance with a sensitivity of $0.2 \mu\text{g}/\text{cm}^2$, (ii) differential manometers system, and (iii) automatic recording volumetric apparatus at constant pressure. The results have been supplemented by photomicrography.

Impurities diffusion of silver in aluminium has been studied at temperature interval $400-600^{\circ}$.

The oxidation of dysprosium metal foils have been studied in the temperature region $500-800^{\circ}$ and at an oxygen pressure of 100 mm of mercury. The oxidation kinetics can be described by means of the parabolic rate equation. A plot of parabolic rate constant vs $1/T$ gives a straight line and corresponds to an activation energy of 24.76 K cal/mole . Experiments with radioactive marker indicate that the marker remains at oxide/oxygen interface. Photomicrograph of a metal foil oxidised to completion at 800° show that it splits into two sections parallel to the surface and the ends are curled apart.

This is due to redistribution of the stress present at the metal/oxide interface and is consistent with the mechanism of growth of Dy_2O_3 through the inward diffusion of oxygen ions through the oxide layer.

SOLUTION CHEMISTRY

Thermodynamic Properties of Solutions (1963) (Dr.P.R. Chaudhary)

Construction of a precision ultrasonic interferometer for measurement of adiabatic compressibility and apparent molal properties of some solutions.

The study of thermodynamic properties provide valuable information for understanding solid and liquid state properties. Such data are required in design engineering. A precision ultrasonic interferometer is being developed to find out

In this instrument, spurious dips have severely been restricted by using a 5-MC X-cut crystal and a quartz transmission plate with optically flat faces. The reflection error has been arrested by confining the measurements in Fresnel diffractional zone and using a large reflector which intercepts most of the principal beam. The electronic circuit uses a RF bridge consisting of three 52 ohm resistors and the fourth arm is the cell. Motion of the reflector in the cell changes the impedance of this arm of the bridge. The bridge output is rectified and compared to the rectified and attenuated bridge input in a balanced DC difference amplifier. A pulse is produced in the plate circuit of the DC amplifier as the reflector passes through the nodal positions and the nodes are counted in a mechanical counter. The half wave length is measured by means of a 100-mm scale having 0.1 mm rulings viewing through a microscope fitted with a micrometer eye piece. The wave length can be measured with ± 1 micron accuracy. The half wave length is averaged out from about 400 counts and velocity is computed as the product of frequency and wave length. The velocity in water has been determined with this instrument as 1497.00 m/sec which is comparable with recent published values. Further ^{work} is being carried out with solution of carboxy methyl cellulose.

RADIATION AND NUCLEAR CHEMISTRY

1. Nuclear Resonance Absorption - Mossbauer Effect (1965) (Dr.H.B. Mathur)

Application of Mossbauer effect to chemistry.

Two cubic ferrites containing ferrous ion at only one type of site in the spinal structure i.e. tetrahedral (A) in FeCr_2O_4 and Octahedral (B) in GeFe_2O_4 are prepared by solid-solid reaction and their Mossbauer spectra studied with the constant velocity drive apparatus in which Co^{57}/Cu source is

moved with respect to the absorber. The data are summarized in table given below:

Source at 25°					
S.No.	Absorber	Absorber temp.	Isomer shift w.r.t. stainless steel (mm/sec.)	Quadrupole splitting (mm/sec.)	Line width (mm/sec.)
1.	FeCr_2O_4	150°	0.94 \pm 0.04	-	0.80 \pm 0.04
		120°	0.92 \pm 0.04	-	0.80 \pm 0.04
		100°	0.94 \pm 0.04	-	0.82 \pm 0.04
		25°	0.96 \pm 0.04	-	1.04 \pm 0.04
2.	GeFe_2O_4	-184°	1.18 \pm 0.04	2.70 \pm 0.04	-
		100°	1.17 \pm 0.04	2.86 \pm 0.04	-
		25°	1.20 \pm 0.04	2.80 \pm 0.04	-

The Mossbauer spectra show that (1) in FeCr_2O_4 , the tetrahedral site symmetry is non-cubic at room temperature even though the bulk symmetry as determined by x-ray is cubic, (2) the observed quadrupole splitting of FeCr_2O_4 viz. 2.70 \pm 0.04 mm/sec at -184° is due to creation of an electric field gradient on the tetragonal (c/a < 1) distortion of the lattice at that temperature.

Fe^{2+} ion in GeFe_2O_4 is less covalent than in FeCr_2O_4 due to the presence of Ge^{4+} ions at the neighbouring site which form strong co-valent bonds with oxygen and hence decrease the electron density around Fe^{2+} ion.

The quadrupole splitting in GeFe_2O_4 is due to the presence of a strong non-cubic field (probably trigonal) at the β sites in the spinal structure.

Radiation Effect on Materials (1964) (Dr.H.B. Mathur)

To study the effect of gamma-radiation on materials and reactions.

The effect of temperature and metal ions Fe^{2+} , Fe^{3+} , Ag^{2+} , UO_2 and Ce^{4+} on the yield of naphthol in the radiolysis of

The 'G' value of naphthol in the radiolysis of a solution of tetrahydrofuran + water + solid sodium nitrate (NaNO_3) does not show any improvement. High temperature ($230-240^\circ$) and high pressure radiolysis of a mixture of naphthalene (at 3 atmospheres) and water vapour (at 30 atmospheres) for one hour increases the 'G' value for naphthol to nearly 25. Detailed work is in progress.

CATALYSIS

Nickel Catalyst for Hydrogenation (1958) (Dr.A.B. Biswas)

Under controlled experimental conditions a basic nickel carbonate with low temperature of reduction and giving products (Ni) of high surface area has been obtained. This, however, cannot be wet-reduced in oil below 250° . It is found necessary to co-precipitate some copper carbonate along with nickel carbonate in order to obtain active wet-reduced catalyst. Series of mixed carbonates of copper and nickel have been prepared in various proportions, which are reduced to active nickel copper catalyst by heating them in oil at 250° for two hours. The x-ray powder patterns are taken and from them 'd' and 'a' (unit cell dimension) are calculated.

A semi-micro hydrogenation kinetics unit, set up earlier, is being used to study and compare the condition for wet reduction in oil for the active catalysts prepared from imported nickel formate and from coprecipitated copper-nickel basic carbonates. It is found that the copper-nickel catalysts containing 20-38% copper are substantially more active than the imported readymade catalysts. These are also almost as active as the catalyst supported on silica, with the added advantage that these can be prepared in oil below 250° , whereas the latter are reduced in the dry state at high temperatures of 500° .

Transition metal ions are known to exhibit interesting surface properties as well as catalytic activities by virtue of the presence of unpaired electrons. A project has been initiated to investigate the electronic and magnetic properties of such catalysts with a view to correlate them with their catalytic activity. A high vacuum unit has been designed and is being fabricated and tested.

PHYSICAL CHEMISTRY OF MICROMOLECULES

1. Physicochemical Properties of Indian Silk 1963) (Dr.A.B. Biswas) (1962) Dr.P.R. Chaudhary)

A study has been undertaken to determine the structure of Indian silk and relating it with its physical and mechanical properties. This will be useful in suggesting better processing conditions and improving their keeping qualities etc.

Previous study of Mysore pure silk fibroin has been extended to Mysore cross-breed, Eri and Tussah (M.P.) varieties. All the three varieties of fibroin indicate that sericin is bound The solubility and stability studies in water of more strongly to fibroin in Eri and Tussah than in Mysore pure and cross-breed varieties.

Hydrogen ion equilibrium studies are carried out at four different temperatures from which pK intrinsic for dissociating groups and heats of dissociation are being computed. An analysis of the titration data indicates that the maximum net positive charge on the protein fibre in extreme pH is 14, 55 and 40 respectively for Mysore cross-breed, Tussah and Eri fibroins. This is in good agreement with the amino acid analysis of these fibroins reported in the literature.

The solubility of Mysore pure fibroin in lithium bromide solutions of different concentrations have been studied. The

The shape and size of the fibroin are being studied by viscosity and light scattering measurements.

2. Degradation of Long Chain Molecules by Ultrasonics (1962) (Dr.P.R. Chaudhary)

The study of the degradation of polymers is of great interest both in its fundamental and applied aspects. The ultrasonic degradation has some resemblance to the mechanical degradation, e.g. mastication etc. The process is investigated to obtain useful information on different polymers which could be applied in industry.

Work is continued on the degradation of butyl rubber in solution. The kinetics of degradation has been studied by both solution viscosity method as well as by free radical estimation as a function of DPPH consumed. It has been observed that the rate of degradation obtained by the latter method is faster in all cases and this has been attributed to the inherent limitation of the two methods used for the quantitative determination of the number of breaks occurring in the polymer molecules. The effect of viscosity during the degradation of molecules is being carried out. As expected, the rate of degradation is reduced as the viscosity of the degrading solution is increased. The cavitation which is responsible for degradation is reduced as the viscosity of the solution is increased.

RARE METAL CHEMISTRY

Organoxy-titanium Compounds (1963) (Dr.J. Gupta)

To synthesize and study new titanium organics with $-(Ti-O-X)-$ linkage.

Basic research on the synthesis of compounds of the above type (X is a polyvalent non-metal such as C, P, S) had been extended to include adducts with nitrogenous bases (ammonia, pyridine etc.).

The reaction between titanium tetrachloride and dimethyl sulphate is studied further and a reactive monochloro intermediate of the composition $ClTi(SO_4)(CH_3SO_4)$ is isolated.

powder sensitive to moisture. It reacts easily with actual or potential hydroxylic organic compounds to give stable chlorine-free products with phenol, acetylacetone, salicylaldehyde and methyl salicylate. Dichloro titanium sulphate also forms new sulphates with acetoacetanilide and dibenzoylmethane by complete elimination of chlorine.

A systematic study has been launched on the partly chelated titanium (IV) chlorides with phenolic compounds. Catechol titanium dichloride $C_6H_4O_2TiCl_2$ is found to react with excess of catechol to form the red solid $C_6H_4O_2Ti(C_6H_4O_2H)_2$.

Resorcinol titanium dichloride, however, gives up only one chlorine under similar conditions to form $C_6H_4O_2Ti(C_6H_4O_2H)Cl$. More data are collected to arrive at some generalization on the stereochemical aspects of the covalent linked titanium atom.

Infra-red analysis of some typical ammonia adducts reported earlier is in progress. More ammonia and pyridine adducts have also been prepared. Anhydrous ethylenediamine and quinoline are also found to form adducts with chelated titanium (IV) dichlorides.

The study of reactions between titanium tetrachloride and alkyl phosphates is complicated by the fact that the reaction product is sometimes a mixture of the dichloro and oxo derivatives of the titano-phosphates. A pure oxo-product (not containing OH group) appears to be obtainable by careful hydrolysis of the mixtures, but this needs confirmation. Chelated titanium dichlorides react with alkyl phosphates to give chlorine-free powdery products which are now under study.

2. Diphenyl Dithiophosphinic Acid Complexes (1964) (Dr.J. Gupta)

Relatively little is known on metal complexes bonded through sulphur only. Some compounds of the title acid were prepared. Complexes with Cr(III), Cu(I), Co(III) and Ni(II) were mentioned in the last report.

Reaction between the free acid and titanium tetrachloride in benzene led to the isolation of the solvated red crystalline product $\text{Cl}_2\text{Ti}(\text{S}_2\text{PPh}_2)_2 \cdot 2\text{C}_6\text{H}_6$, which loses the two solvent molecules by heating in vacuum. Stannic chloride similarly yields the pure and solvated dichlorides as yellow products in benzene. Direct addition of alcoholic solution of the acid to aqueous alcoholic solutions of suitable salts has led to the isolation of the compounds AgL , ThL_4 and UO_2L_2 , where LH represents a molecule of the ligand containing one replaceable hydrogen. It is proposed to conclude this work within the year.

COORDINATION COMPOUNDS AND SYNTHETIC INORGANIC CHEMISTRY

1. Semiaromaticity and Isomerism (1963) Dr.D.N. Sen)

Quasiaromaticity of chelated acetylacetone was demonstrated by nitrating and thiocyanating tris-(2,4-pentanediono)aluminium (III). Aluminium nitrate and concentrated nitric acid in acetic anhydride were found to be excellent nitrating agents for some metal acetylacetonates.

In several instances, electrophilic attack of the aromatic part of the chelate ring has been observed. Characterization of reaction products as well as nitration study of ligands and some aromatic compounds are being pursued. Thiocyanation of bis(2,4-pentanediono)beryllium (II) has given a product which is characterized by elemental analysis and infrared spectra as bis(3-thiocyanato-2,4-pentanediono)beryllium (II). Similar work with tris(2,4-pentanediono)manganese (III) has given metal-free, 3-thiocyanato-2,4-pentanedione. Further attempt to isolate 3-nitro-2,4-pentanedione has led only to partial success - although a nitrogen containing low melting solid is isolated, its elemental analysis does not conform to expected values. A few of metal acetylacetonates are found to react with mercuric acetate; the products, however, resemble mercuric acetylacetonate in their infrared spectra.

Copper chelate of acetoacetyl diethylamide is prepared for the first time. The reflectance spectra and x-ray powder patterns of the material and of some orthochloroacetone chelates are being examined. A new compound, monochloro tris-(4-anilido-2,4-butanediono) titanium (IV) having an unusual seven-coordination has been isolated and its infrared spectra are being studied. Several colour isomers of bis-(salicylaldoximato) copper (II) are isolated and their infrared spectra, reflectance spectra and x-ray powder patterns are studied. Calculation of expected 'd' values by using suitable equation and literature data reveals that at least there are two definitely different types of crystal modifications for these colour isomers.

2. Infrared Studies of Werner Type Compounds (1964) (Dr.D.N. Sen)

Infrared spectra of some Werner type complexes e.g. the metal amines and cis-trans isomers were studied.

The work on CsBr prism region has to be repeated. During this period, infrared absorption spectra of some chelates of salicylaldoxime with divalent element are recorded in the NaCl optics region. The hydrogen bonding of these compounds and the ligand is of special interest. Deuteration-cum-solvent studies, besides throwing light on the intermolecular and intramolecular hydrogen bonding in salicylaldoxime has been of help in assigning a peak in the 1600 cm^{-1} region, previously thought by other workers as due to C = N stretching frequency to O-H deformation vibration.

3. Coordination Polymers (1964) (Dr.D.N. Sen)

A number of coordination polymers of the bis-ligand, bis-(8-hydroxy quinolyl)-methane were synthesized.

Systematic study has led to the characterization of two compounds of monooxo bis(8-quinolinolato)titanium (IV), one yellow compound identical with analytical preparation; the other, a new

stable up to 280° and decompose rapidly at 300° and above. reddish brown polymer is a monohydrate and infrared spectra show medium intensity bands at 828 and 802 cm^{-1} presumably due to Ti-O-Ti bonding while the anhydrous yellow compound shows absorption at 830 cm^{-1} which may be assigned to Ti = O stretching vibration. These results have led to believe that in the reddish compound, titanium shows 5-coordination while in the reddish brown compound, it shows 7-coordination.

Work on another interesting bis-ligand, resorcinol 2:4-dihydrate is carried out. Coordination polymers of Cu(II), Ni(II), Co(II) and Zn(II) with this chelate ligand having potential polyfunctional coordination sites are synthesized. The N.M.R. spectra of the ligand in CDCl_3 shows signals at 397.5 cps and 465.5 cps (doublets $J = 9$ cps) which can be assigned to aromatic C-H in positions 5 and 6. The signals at 587 cps and 628 cps represent protons of the two phenolic functions and the signals at 757.5 cps and 761 cps can be ascribed to the two aldehydic groups. Since the starting material is resorcinol, the chelate ligand is thus obviously proved to be resorcinol 2:4-dialdehyde and hence the structures of these coordination polymers could be easily visualized.

4. Phosphors (1959) (Dr.D.N. Sen)

To synthesize and study zinc sulphide and alkaline earth halophosphate phosphors which are finding growing importance.

The methods for the preparation of zinc sulphide phosphor developed some years back are being modified to give pure materials. A few rare earth metal incorporated zinc sulphide and halophosphate phosphors have been prepared. A new column has been designed and assembled for purifying nitrogen. An instrument for measuring fluorescence has been set up and is being used for measuring spectral energy distribution of several phosphors.

Miscellaneous Applied Work

1. Nickel Formate (Dr.J. Gupta)

In a collaborative programme of work with the RRL, Hyderabad, a process for obtaining nickel formate of catalyst grade has been worked out. Laboratory tests carried out so far at the NCL and RRL, Hyderabad have been favourable. A large laboratory sample of about 15 kg. has been prepared for tests by users in the Vanaspati industry.

2. Thionyl Chloride (Dr.J. Gupta)

Details of a process suitable for the laboratory production of thionyl chloride in the Fine Chemicals Project have been worked out.

3. Chromatographic Materials (Dr.D.N. Sen)

Silica gel samples prepared in FCP are comparatively examined with E.Merck's special samples. Fresh samples of silica gel are also prepared and are being examined. A few Fuller's earth samples, available from FCP have been examined. A few samples of ascarite have been prepared and are being examined for suitability. The conventional method of preparation of hydroxylamine from sodium nitrate and sodium sulphide is tried. Spectroscopically pure manganese sesquioxide is prepared on behalf of FCP.

PHYSICO ANALYTICAL CHEMISTRY (Dr.P.R. Subbaraman)

Following are the three main activities of this group: (1) Analytical service for various materials relating to different NCL projects, (2) development of new and specific analytical methods, and (3) basic work to follow up the mechanisms of reactions involved in different analytical procedures.

1. Analytical services (Perm.)

Using classical chemical as well as instrumental methods such as ultra violet and visible spectrophotometry, emission

spectroscopy, flame photometry, polarography and allied electro-analytical techniques, analysis of the following materials has been done: phenoxyacetic acid; malonic acid and calcium malonate; calcium oxide; zinc sulphide and nickel oxide for trace impurities; nickel formate; Raney alloy; lac dye for arsenic and lead; sorbitol for trace contaminants; zinc and cadmium oxides; vanadium in brine for industry; colour standard for butyl phthalate.

2. New methods of analysis (1964)

A new method for microgram levels of vanadium using ferron has been developed. The vanadium-ligand ratio is 1:2 with formation constant of 5.6×10^{-4} at 25° and ionic strength, 0.1 as ascertained from spectrophotometric data. The interesting colour reaction of this chelate with alcohols is not readily explained; a possible interpretation is ester formation between the alcohol and the hydroxyl group of the vanadic acid.

In continuation of the interesting analytical applications of polyphosphates in ion exchange, polarography and titrimetry reported earlier, work is in progress on the complex formation of polyphosphates with Au(III), Ag(I) and Tl(I).

3. The molybdate dimethylglyoxime reaction (1964)

It is proposed to investigate the catalytic reduction of α -dioximes in general, with stannous chloride in presence of molybdate.

Rate studies, isolation and analysis of end products have indicated that dimethylglyoxime is quantitatively reduced in a few hours to ammonia and acetoin with stannous chloride even when the ratio of molybdenum to glyoxime is less than 1:50. Reduction is stepwise through diacetyl. Dimethylglyoxime itself is found to be unstable in dilute hydrochloric acid solution rapidly hydrolysing to diacetylmonoxime and hydroxylamine.

Direct Reduction of Insoluble Vat Dyes in the Solid State at the d.n.e. (1965)

Work reported earlier has been followed up by examining some more dyes e.g. indanthrone, 1-1'-dianthrimide, indanthrene Khaki GG, indanthrene brown BR, indanthrene yellow 3R and indanthrene yellow FFRK. It has been confirmed that the peak potentials of reduction like the half-wave potentials from solution are reproducible under the experimental conditions and are generally more negative than the half-wave potentials. The thermodynamic significance, if any, of the peak potentials is not clear and is under investigation.

FLUORINE CHEMISTRY

Preparation of Organic & Inorganic Fluorides (1963) (Dr.V. Damodaran)

Use of various fluorinating agents in the preparation of organic and inorganic fluorides is being studied.

Potassium hexafluoroantimonate, KSbF_6 , seems to be a convenient laboratory reagent for replacing moderately reactive chlorine atoms. Sodium silicofluoride showed some activity in this direction. A vapour/solid reaction between chloroform and potassium fluoride led to only 5% fluorination. Arsenic trifluoride was found to be a very active fluorinating agent (F for Cl) but it is very toxic and volatile.

Three new halogenated aliphatic compounds (hitherto unreported) have been prepared. These are chloral condensation products of acetylacetone and dibenzoylmethane and a compound believed to be the di-O-acetate of 1,1-dibromo,2,2-dihydroxy ethane. All these compounds are analyzed correctly, but with the fluorinating agents at our disposal now it may not be possible to fluorinate them satisfactorily.

Potassium hexafluoromanganate is found to decompose on heating to ca. 600° in a current of dry air to give a mixture of potassium fluoride and an oxide or oxyfluoride of manganese.

Further studies on this and similar compounds are in progress.

far appears to be either identical or very similar to trichomy.
Further work is in progress.

D) Carbohydrates (Dr. J.L. Bose)

1. Cellulose caprate (1963)

This work has been undertaken at the instance of the Defence Department. The object is to prepare cellulose caprate with requisite degree of substitution for use as the main ingredient of an optical cement composition imported at present.

The conditions for the preparation of cellulose caprate having the required degree of substitution have been standardized and a few laboratory-scale batches of the compound are prepared. Attempts have been made to simplify the process which have met with success. The economics of the process is studied.

It is proposed to prepare cellulose caprate in larger batches and then prepare the optical cement, after procuring the two plasticizers required to be incorporated in small quantities. The cement will be sent to the Defence Department for trials.

2. Modification of indigenous gums for use as substitutes for gum arabic (1962)

The work is undertaken at the instance of the Indian Posts & Telegraphs Board. The aim is to evolve a suitable substitute for gum arabic by modifying easily available indigenous gums. Presently, imported gum arabic is used by the Post & Telegraph Department for general adhesive purpose and for making teleprinter papers.

Some of the indigenous gums like ghatti, jeol, karaya and cashew have been examined. Several methods of modifications are employed. Two samples of modified gum have been sent to the Post and Telegraphs Board, New Delhi, for testing and the report is encouraging. A new method for the modification of some of these gums has been developed which gave samples with satisfactory adhesive properties as compared with gum arabic. Three of these modified gum samples have been sent to Post and Telegraphs Board for testing and the results are awaited.

It is proposed to modify other indigenous gums by this method. With a view to apply the method more effectively, attempts will be made to correlate the structural modifications involved in the process with changes in the adhesive property.

3. Studies in indigenous gums (1965)

Studies have been undertaken to investigate the structure of the gum from Terminalia tomentosa with a view to suggest its proper utilization.

Preliminary studies in the identification of the component sugar units have been carried out.

4. Utilisation of groundnut shells for the production of dissolving pulp and vanillin (1962)

The work on the utilization of groundnut shells, which constitute a huge agricultural waste of India, was taken up after it was discovered in this laboratory that groundnut shell lignin is quite different from the tropical wood lignin in giving mainly vanillin, uncontaminated with syringic aldehyde, on oxidative cleavage. The work on pulping of the groundnut shells was also taken up for the proper utilization of the cellulosic part.

Vanillin has been prepared from groundnut shells or lignin isolated therefrom by using various oxidizing agents under different conditions. Optimum conditions for oxidation with alkaline nitrobenzene have been established but the process is found to be uneconomical for the production of vanillin directly from the groundnut shells. A dissolving pulp is also prepared from the groundnut shells in satisfactory yields. The pulp is found to be suitable for the preparation of carboxymethyl cellulose (CMC). Some other aromatic nitro compounds have also been used for the oxidation of groundnut shells with a view to obtain marketable byproducts in the reaction. These attempts, however, have not given satisfactory results so far.

A modified method has been developed for the preparation of CMC from moist groundnut shell pulp without making sheets.

It is proposed to get groundnut shell pulped by the sulphite method at the Bengal Paper Mills and use the ligno-sulphonic acid for oxidation to vanillin and simultaneously obtain a pulp which would be further processed for the preparation of CMC. This work has been carried out in collaboration with the Rayon Grade Pulp Project group.

E) Plant Pigments (Dr.K. Venkataraman)

1. 2,2-Dimethylchromenes (1962)

A general method is being developed for the synthesis of 2,2-dimethylchromenes, a type of which there are many representatives in nature. Attempts at synthesizing 5,7-dihydroxy-2,2-dimethylchromene have so far been unsuccessful, probably because of the tendency of this compound to tautomerize to a quinone-methide or undergo other changes. Incidentally, it is an interesting fact that the naturally occurring 2,2-dimethylchromenes, if they possess the hydroxyl group in the 7-position, also carry a carbonyl group in the adjacent position; chelation of the hydroxyl and carbonyl groups apparently stabilizes the compounds. Evodionol methyl ether (6-acetyl-5,7-dimethoxy-2,2-dimethylchromene) has been synthesized, and the synthesis of alloevodionol (8-acetyl-7-hydroxy-5-methoxy-2,2-dimethylchromene) is in progress.

2. NMR studies of phenolic ketones (1965)

From the point of view of the identification of degradation products of flavonoids, the behaviour of phenolic ketones in the Baker-Venkataraman transformation, and the chemical shifts of aromatic protons as the result of chelation, the NMR spectra of a series of phenolic ketones are being determined. In connection with work on the mechanism of direct formation of flavones in the Baker-Venkataraman transformation, NMR studies are being carried out on keto-enol equilibria in dibenzoylmethanes and on possible intermediates, such as 2-hydroxy-

3. Flavones from iretol (1964)

The synthesis of 2,4,6-trihydroxy-5-methoxyacetophenone and 2,4,6-trihydroxy- ω -5-dimethoxyacetophenone by the Hoesch reaction was mentioned in the last Annual Report. Using the former hispidulin (dinatin) has been synthesized and the synthesis of several other naturally occurring flavones and flavonones is in progress.

4. Pigments of Garcinia species (1958)

In view of the unique structure of morellin, the work is being extended to other Garcinia species. The structure of gambogic acid suggested by Yates on the basis of the structure of morellin has been confirmed by Ollis, but the stereochemistry of the side-chain carrying the carboxyl group was not established. This has now been done in the light of the chemical shift of the vinyl proton in the side-chain, and it has been shown that gambogic acid corresponds to morellic acid and acetyl gambogic acid to isomorellic acid. Other aspects of the chemistry of gambogic acid in relation to the morellins and morellic acids are under study. New pigments have been isolated from Garcinia morella and their structures are under investigation. The structures of various degradation products of morellin and octahydromorellin are also being determined, mainly on the basis of mass spectra and NMR spectra.

5. Hydroxyanthraquinones (1964)

1,3,6-Trihydroxyanthraquinone has been synthesized, and the synthesis of colucidin (the 2-methyl derivative) is in progress. The synthesis of rhodocladonic acid is in progress. As a model compound for comparison with lac pigments, 1,2,4,6-tetrahydroxyanthraquinone-7,8-dicarboxylic acid is being synthesized.

F) Essential Oils (Dr.S.C. Bhattacharyya)

1. Vetiver oil (1958)

The tricyclic sesquiterpene primary alcohol, $C_{15}H_{24}O$, containing one exomethylene double bond, were shown to have a new carbon skeleton, the $-CH_2OH$ group being attached to a cyclopentane ring, fused to two other rings. Work on the primary and secondary alcohols occurring in the oil is in progress.

A new laevo-rotatory alcohol khusinol oxide, $C_{15}H_{24}O_2$, isolated from North Indian vetiver oil is shown to possess the structure and stereochemistry (I). It also belongs to the antipodal group.

On the basis of chemical and spectral evidences, khusinodiol, the main product obtained by BF_3 -treatment of khusinol (III), has been assigned the stereostructure (II). The hydrocarbon, a minor product of the above reaction is shown to be (IV). The diene-monol (V) (+) α -cadinol (VI), and isokhusinol (VII) have been prepared from khusinol. (See figures I to VII on p.58).

2. Costus root oil (Kashmir variety) (1958)

The acid (I) obtained by the metal amine reduction of solid dihydrocostunolide (II), on treatment with acetic acid and perchloric acid gave santanolide 'c' (III) as the main product, the formation of which confirms the assignment of stereochemistry at C_4 in (I). Characterization of other products is in progress.

The monoepoxide from (I) has been subjected to acid catalyzed cyclization with interesting results.

The diepoxide (IV) obtained from (II) is identical with the monoepoxide (IV) of dihydroparthenolide (V) from which the stereochemistry of parthenolide (VI) at C_6 , C_7 and of dihydroparthenolide at C_6 , C_7 and C_{11} follows. This identity also confirms the revised structure (VI) assigned to parthenolide.

The structure (VII) of the ketocarboxylic acid, has been revised to the structure (VIII) on the basis of results of bromination and subsequent dehydrobromination, when a cross-conjugated ketocarboxylic acid ester (IX) is obtained, the structure of which is supported by IR, UV and NMR spectra (See figures on p.58).
I to IX

3. Valerian root oil (1960)

The valerian root oil (concrete) from adjoining areas in the Himalayan regions is subjected to steam distillation and the distillates separated into acidic and neutral parts. The acidic portion contains, isovaleric and caproic acids. The neutral portion and the steam non-volatile part are being examined.

4. Essential oil from Nardostachys jatamansi DC (Valerianaceae) (1963)

In addition to the earlier reported compounds, a new oxide, hydrocarbons, a polyoxygenated crystalline solid (m.p. $77-78^\circ$), together with β -eudesmol (I), elemol (II) and angelicin (III) have been isolated from the greyish brown variety of Nardostachys jatamansi. Structural elucidation of the polyoxygenated crystalline material is in progress. Another vasodilatory agent (+)-visnadin (IV) has been prepared from jatamansin in addition to the previously reported (+)dihydrosamidin.

In continuation of the work on the dark brown variety of Nardostachys jatamansi, an α , β -unsaturated aldehyde, and an alcohol, $C_{15}H_{26}O$, have been isolated. Structural investigations of these compounds are in progress. (See figs. I to IV on p.59).

5. Turmeric oil (1963)

A convenient method for the preparation of (+)ar-turmerone from turmerone has been developed.

(+) α -Curcumene (I), free from the isopropenyl isomer (II), has been synthesized by two different routes. The acid (III) related to nuciferol (IV) has been synthesized. (See figs. I to IV on p.59).

6. Oil from Cyperus Scariosus (1964)

A new crystalline sesquiterpenic ketone, isopatchoulenone, $C_{15}H_{22}O$, m.p. 48° , has been isolated from the ketonic fraction of the essential oil obtained from the tubers of Cyperus scariosus. On the basis of spectral and chemical evidences structure (I) has

been assigned to isopatchoulenone. Isopatchoulenone has been prepared from cyperene (II) by oxidation with t-butyl chromate. Further work is in progress. (See figs. I to II on p.59).

7. Oil from the roots of Inula racemosa (1965)

Roots of Inula racemosa (from Jammu) are extracted with petroleum ether in the usual way to get an oil in 6% yield. The oil is being processed for chemical examination and isolation of the constituents. Two main constituents are alanto and iso-alanto lactones.

8. Black dammar resin (1958)

In addition to the compounds reported earlier, three new triterpenes oxidodammarol (I), epi-4-taraxastane diol (II) and the keto-monol (III), have been isolated and their structures established on the basis of chemical and spectral evidences. (See figs. I to III on p.60).

G) Medicinal Plants (1964) (Dr.N.L. Dutta)

After the successful completion of the sponsored project on isolation of berberine hydrochloride from berberis bark, work on the preparation of neutral berberine sulphate has been undertaken along with the preparation of acid sulphate. It is believed that these two berberine derivatives are having medicinal properties and are in good demand. A sample of acid sulphate (25 g.) has already been sent to the party for evaluation. Work on the preparation of neutral type is in progress.

ORGANIC REACTIONS AND SYNTHESIS

A) Studies of Typical Reactions Effecting Structural Transformations (Dr.S.C. Bhattacharyya) (1960)

1. Compounds related to selinane and elemene

Junenol, dihydrojunenol, tetrahydroaussurea lactone, epidihydroeudesmol (I) and the ketodicarboxylic acid (II) related to elemene have been synthesized. The absolute configuration of

elemol (III) has been established. A number of esters of 3, α -hydroxy santanolide 'c' (IV) have been prepared and their elimination reactions studied. This has led to improved methods for the preparation of sant-3-enolide, sant 4-(14) enolide and santanolide 'c' from santonin. Eudesmol has also been converted to santanolide 'c'.

Tetrahydroelemol (V), elemene, 2,3,12-trioic acid (VI) and elemene, 2,3,12-triol (VIa) have been synthesized. Improved methods for the preparation of keto-ketal (VII), an important intermediate for triterpene synthesis, have been developed. This has been converted to the dacalone (VIII). The synthesis of the decalone (IX) is in progress.

Tetrahydroelemol (V) and dihydroeudesmol (I) on treatment with acetic acid and perchloric acid give a mixture of hydrocarbons (X and XI) by dehydration followed by migration of the double bond inside the ring. The resulting hydrocarbons, by a series of reactions have been converted into 6 and 8 elemenones (XII and XIII) and 6 and 8 selinanones (XIV and XV). (see figs. I to XV on p.60).

2. Compounds related to guaiol (1965)

Solid dihydroguaiol obtained by catalytic hydrogenation of guaiol has been converted into hexahydrodehydrocostus lactone by a series of reactions.

3. Transformations in the longifolene series (1964)

Longifolic acid obtained during the oxidation of longifolene has been converted into a series of compounds including half esters and their degradation products.

4. Transformation products of tricycloekasantalic acid (1958)

By application of Wittig's reaction at some of the stages, tricycloekasantalic acid has been converted into optically pure α -santalene (I) α -santallic acid (II) and α -santalol (III). (see figs. I to III on p.61).

5. Synthetic approach in santalene-longifolene series (1964)

Isobicycloekasantalic acid (V) obtained as one of the products of dehydrohalogenation of bicycloekasantalic acid has been synthesized from camphene (I).

Camphene is converted to the allylic alcohol (II) by Prins reaction. This on bromination, cylation and hydrolysis gave isobicycloekasantalic acid (V). Both the optically active forms of the acids have been synthesized. The acid (V) is being used to synthesize iso- β -santalene (VI) for comparative odour evaluation in the series. The study of stereochemistry of the lactone (VII) prepared earlier is in progress. (See figs. I to VII on p.61).

6. Base catalysed reactions of lithioethylenediamine (1961)

This isomerisation is being applied to steroids and medium sized ring compounds with interesting results.

7. Selenium dioxide oxidation of terpenes (1964)

2,6-Dimethyl octene-2, α -santalene, β -santalene and tetrahydro β -elemene gave a mixture of the corresponding alcohols and the α, β -unsaturated aldehydes. The mixtures on further reduction has given the alcohols 2,6-dimethyl octene-2-ol, α -santalol, β -santalol and the alcohol (I). (See fig. I on p.61).

8. Bergamotenes (1964)

The synthesis of cis-nor bergamotinic acid (I), a key intermediate in the synthesis of α - and β -bergamotenes (II) has been described earlier. The synthesis of the model compound pinene (III a, b) is carried out using pinic acid (IV, R=H) as the starting material. The diethyl ester of pinic acid (IV, R=E_t) on acyloin condensation gives a mixture of two acyloins (V). The tosylate of the latter on reduction with LAH give the alcohol which could be oxidised to nopinone (VI) separated and purified by crystallisation of a suitable derivative.

Review papersSurvey & Information

72. Mathur, H.H., and Shastri, D.K., Ultramarine Blue, Paint India Annual, 1957, 67-70.
73. Banerjee, S.C., Synthetic detergents from fatty acids, Indian Soap, Jr., 1957, 22, 257-261.

PAPERS COMMUNICATEDChemical Engineering

1. Doraiswamy, L.K., Bijawat, H.C., and Kunte, M.V., Fluidized Bed Chlorination of Ilmenite - Kinetics of the Preferential Chlorination of Iron, Chemical Engineering Progress, U.S.A.
2. Kunte, M.V., and Doraiswamy, L.K., Estimation of Gaseous Densities, Chemical & Process Engineering, UK.
3. Banerjee, S.C., and Doraiswamy, L.K., Thermodynamic Properties of Vinyl Chloride, British Chemical Engineering, UK.
4. Brahma, P.H., Doraiswamy, L.K. and Pai, M.U., A process study of the Polymerization of Vinyl Chloride, J. Appl. Chem.
5. Narsimhan, G., On the order of a homogeneous irreversible reaction, Canadian Journal of Chemistry, Canada.

Organic Chemistry

6. Bose, J.L., and Dutta, N.L., Isoflavones - Part II - A new synthesis of isoformononetin and daidzein, J. sci. industr. Res.

Physical Chemistry

7. Banerjee, B.C. and Goswami, A., The effect of chloride ions on the orientation of nickel, Electrochem Soc.
8. Banerjee, B.C., and Goswami, A., Structure of electrodeposited nickel, J. Electrochem. Soc.
9. Goswami, A., Structure of iron and chromium deposited on copper single crystals, Trans. Faraday Soc.
10. Goswami, A., Extra reflections by dynamical scattering, J. sci. industr. Res.

Review papers

Survey & Information

72. Mathur, H.H., and Shastri, D.K., Ultramarine Blue, Paint India Annual, 1957, 67-70.
73. Banerjee, S.C., Synthetic detergents from fatty acids, Indian Soap, Jr., 1957, 22, 257-261.

PAPERS COMMUNICATED

Chemical Engineering

1. Doraiswamy, L.K., Bijawat, H.C., and Kunte, M.V., Fluidized Bed Chlorination of Ilmenite - Kinetics of the Preferential Chlorination of Iron, Chemical Engineering Progress, U.S.A.
2. Kunte, M.V., and Doraiswamy, L.K., Estimation of Gaseous Densities, Chemical & Process Engineering, UK.
3. Banerjee, S.C., and Doraiswamy, L.K., Thermodynamic Properties of Vinyl Chloride, British Chemical Engineering, UK.
4. Brahme, P.H., Doraiswamy, L.K. and Pai, M.U., A process study of the Polymerization of Vinyl Chloride, J. Appl. Chem.
5. Narsimhan, G., On the order of a homogeneous irreversible reaction, Canadian Journal of Chemistry, Canada.

Organic Chemistry

6. Bose, J.L., and Dutta, N.L., Isoflavones - Part II - A new synthesis of isoformononetin and daidzein, J. sci. industr. Res.

Physical Chemistry

7. Banerjee, B.C. and Goswami, A., The effect of chloride ions on the orientation of nickel, Electrochem Soc.
8. Banerjee, B.C., and Goswami, A., Structure of electrodeposited nickel, J. Electrochem. Soc.
9. Goswami, A., Structure of iron and chromium deposited on copper single crystals; Trans. Faraday Soc.
10. Goswami, A., Extra reflections by dynamical scattering, J. sci. industr. Res.
11. Trehan, Y.N. & Goswami, A., Thermal oxidation of copper (100) and (111) faces, Trans. Faraday Soc.
12. Trehan, Y.N., and Goswami, A., Twinning and change of crystal orientation, Acta Cryst.

13. Trehan, Y.N., and Goswami, A., Random abrasion of copper (110) face, J. sci. industr. Res.
14. Kuber, M.V., Kulkarni, S.B., and Biswas, A.B., On the phase equilibria of p,p' DDT in binary systems, Zeits. Phys. Chemi.
15. Kulkarni, S.B., Biswas, A.B., and Kuber, M.V., Studies on the linear rate of crystallisation of DDT from supercooled binary melts, Part I, J. sci. industr. Res.
16. Guru Moorti, V.R., and Gharpurey, M.K., Comparative study of the effects of silver precoats on the texture of zinc and cadmium films condensed from vapour in vacuo, Optik.
17. Lakhbir Singh, A new approach to the diamagnetic anisotropy of benzene-the anisotropy of π electrons, Trans. Faraday Soc.
18. Lakhbir Singh, The colour problem of ruby, Nature.
19. Lakhbir Singh, Classical approach to the structure of condensed-ring aromatic compounds - a rejoinder to the problem of dibenzo (cd, mn) pyrene, Can. J. Chem.
20. Narasinga Rao, M.S. and Hira Lal, Metal-protein interaction in buffer solutions, Part II - A polarographic study of the interaction of Zn^{II} , and Cd^{II} with native and modified bovine serum albumins, J.A.C.S.
21. Narasinga Rao, M.S. and Hira Lal, Metal-protein interaction in buffer solutions - Part III - The interaction of Cu^{II} , Zn^{II} , Cd^{II} , Co^{II} , and Ni^{II} with native and modified bovine serum albumins, J.A.C.S.
22. Sharma, B.D., and Biswas, A.B., An X-ray diffraction study of n-alkyl malonic acids, J. Analytical Chem.
23. Jose, C.I., and Biswas, A.B., Measurement of refractive index increment for molecular weight determination by light scattering, J. Polymer Sci.

Plastics & Polymers

24. Kapur, S.L., and Gundiah, S., Anomalous behaviour of polymer solutions. II - Viscosity behaviour of rubber solution at high dilutions, J. Colloid Science.
25. Kapur, S.L., and Gundiah, S., Polymer Solution. III - Viscosity behaviour of dilute solutions of natural rubber in mixed solvents, Die Makromole, Chemic.
26. Kapur, S.L., and Gadkary, S.D., Chain transfer in solution polymerisation IV. Acrylates, J. sci. industr. Res.

5. Synthetic approach in santalene-longifolene series (1964)

Isobicycloekasantalic acid (V) obtained as one of the products of dehydrohalogenation of bicycloekasantalic acid has been synthesized from camphene (I).

Camphene is converted to the allylic alcohol (II) by Prins reaction. This on bromination, cylation and hydrolysis gave isobicycloekasantalic acid (V). Both the optically active forms of the acids have been synthesized. The acid (V) is being used to synthesize iso- β -santalene (VI) for comparative odour evaluation in the series. The study of stereochemistry of the lactone (VII) prepared earlier is in progress. (See figs. I to VII on p.61).

6. Base catalysed reactions of lithioethylenediamine (1961)

This isomerisation is being applied to steroids and medium sized ring compounds with interesting results.

7. Selenium dioxide oxidation of terpenes (1964)

2,6-Dimethyl octene-2, α -santalene, β -santalene and tetrahydro β -elemene gave a mixture of the corresponding alcohols and the α, β -unsaturated aldehydes. The mixtures on further reduction has given the alcohols 2,6-dimethyl octene-2-ol, α -santalol, β -santalol and the alcohol (I). (See fig. I on p.61).

8. Bergamotenes (1964)

The synthesis of cis-nor bergamotinic acid (I), a key intermediate in the synthesis of α - and β -bergamotenes (II) has been described earlier. The synthesis of the model compound pinene (III a, b) is carried out using pinic acid (IV, R=H) as the starting material. The diethyl ester of pinic acid (IV, R=E_t) on acyloin condensation gives a mixture of two acyloins (V). The tosylate of the latter on reduction with LAH give the alcohol which could be oxidised to nopinone (VI) separated and purified by crystallisation of a suitable derivative.

Treatment of nopinone with methyl lithium gives a tertiary alcohol (VII) which with thionyl chloride and pyridine gives α -pinene (IVb) as one of the products from which pure α -pinene is obtained by chromatography. β -Pinene (IVa) is then obtained by Wittig's reaction.

Another route for the synthesis of nopinone from cis-norpinic acid has been undertaken. (See figs. I to VII on p.61).

9. Macrocyclic musk compounds (1961)

In connection with large scale preparation of exaltone and exaltolide, 52 kg. of mustard oil is trans-esterified to get 54 kg. of fatty acid esters. 8 kg. of dihydroxybehenic acid ester and 23.3 kg. of sodium paraperiodate are prepared and partly converted to metaperiodate as required for further reaction.

A method for the reduction of acyloins with hydriodic acid in boiling acetic acid has been standardized. The yield of the ketone (exaltone or dihydrocivetone) by this method is up to 70%. This eliminates the serious difficulty encountered in the reduction of macrocyclic acyloins.

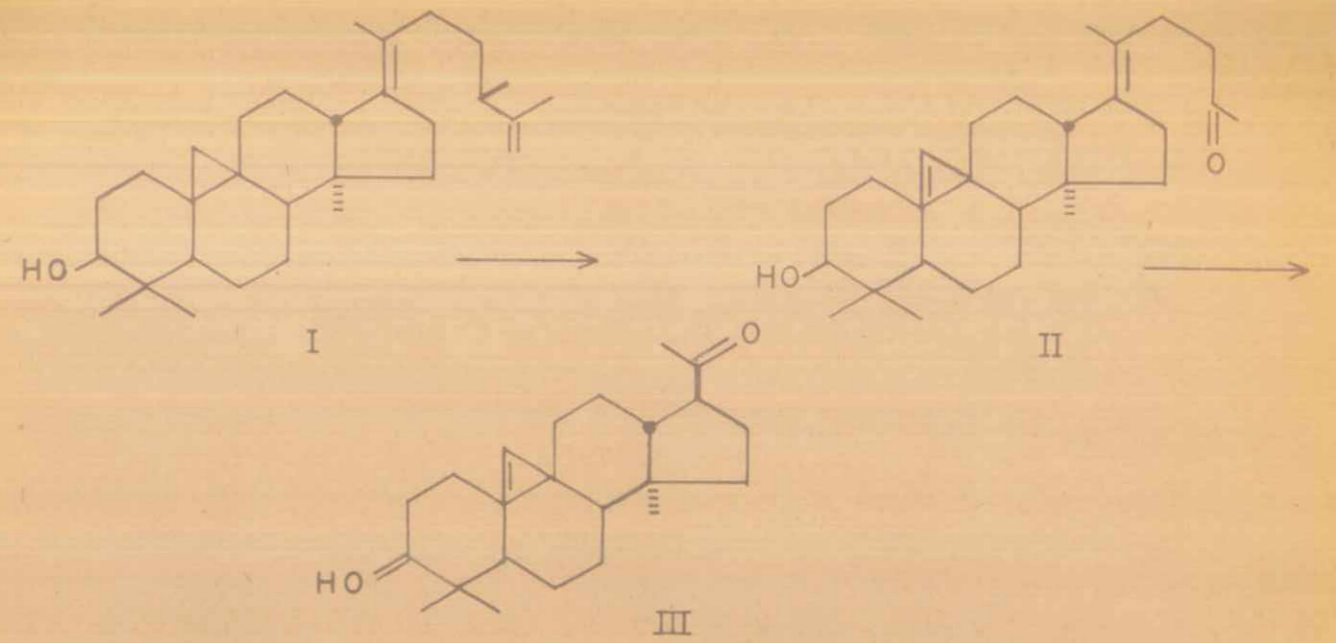
10. Polyesters as stationary phases in GLC (1963)

The effect of spacing of methylene groups in dicarboxylic acid fragment has been reported earlier. The spacing of methylene groups in glycolic fragment has been critically examined and the relation found to be linear again. The constant C in the formula

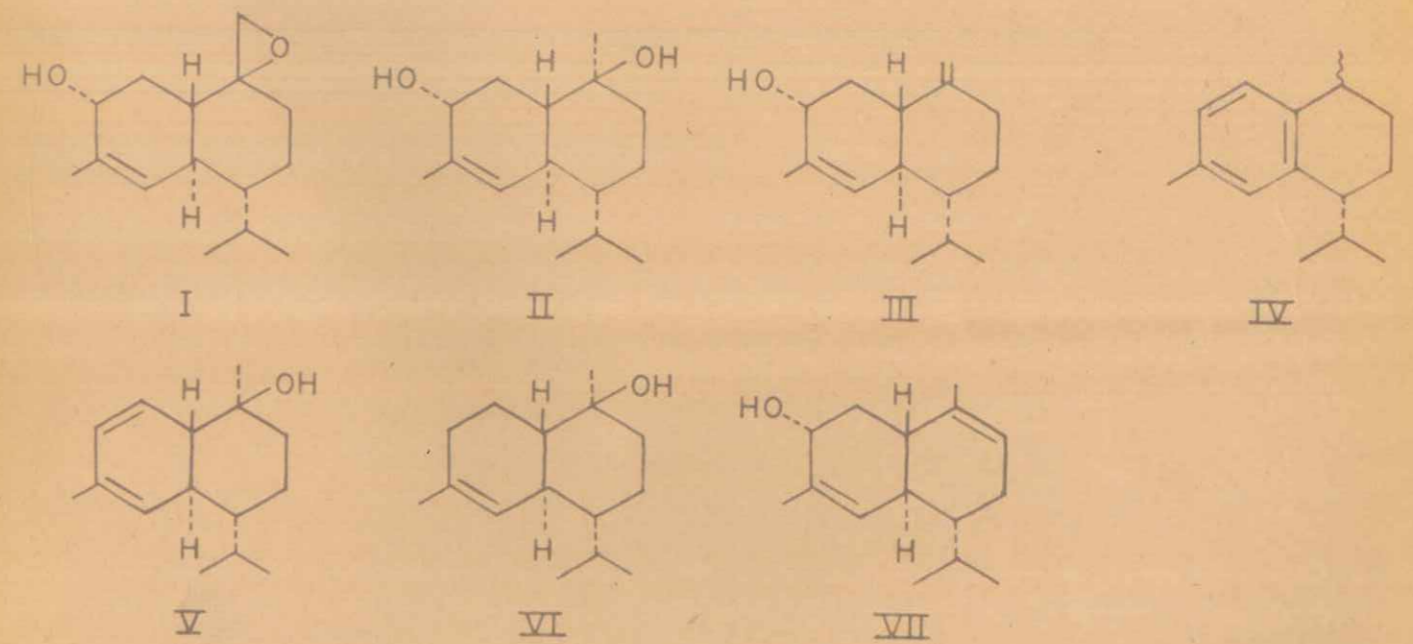
$$C = \frac{\text{tr}^x - \text{tr}^y}{x - y}$$

is different from the constant C, for the spacing of methylene groups in dicarboxylic acid fragment of the polyester. On the basis of these routes, it is now possible to prepare 'tailor made polyester stationary phases' for specific separations which hitherto have not been found feasible.

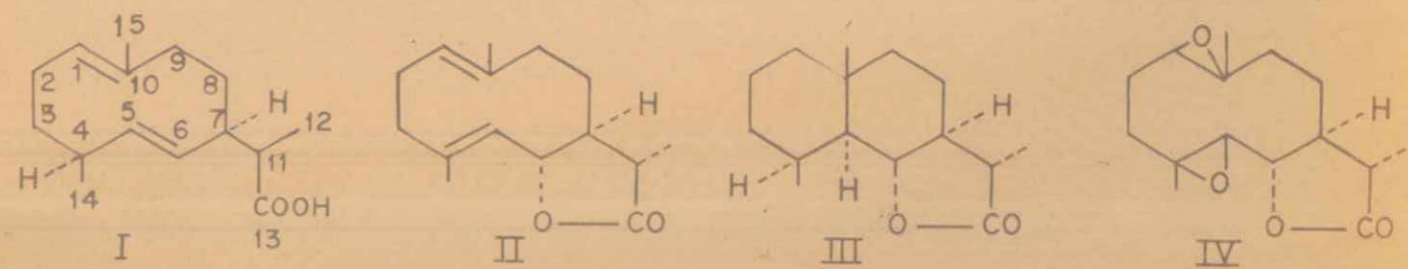
MODIFICATION OF CYCLOLAUDENOL (P. 62)

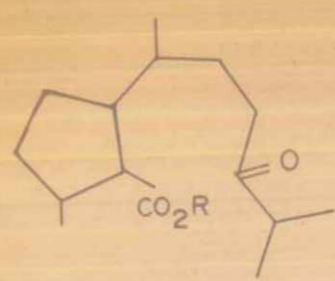


VETIVER OIL (P. 52)

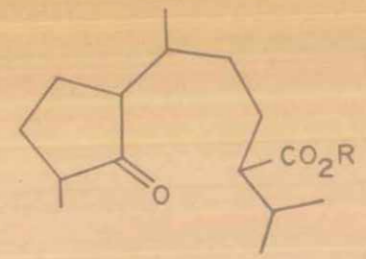


COSTUS ROOT OIL (KASHMIR VARIETY) (P. 62)

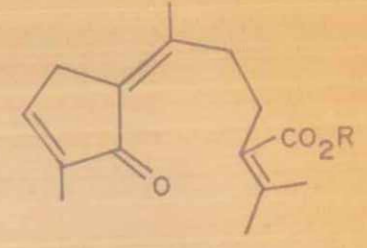




VII (R = H
= CH₃)

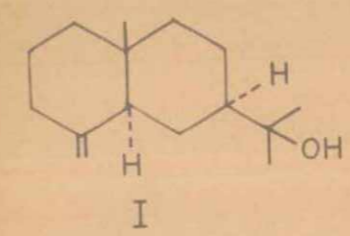


VIII (R = H
= CH₃)

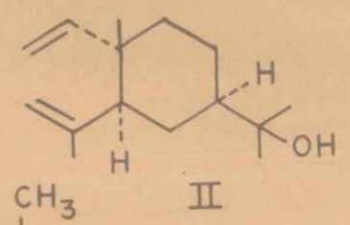


IX (R = H
= CH₃)

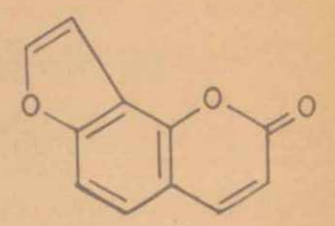
NARDOSTACHYS JATAMANSI (P. 53)



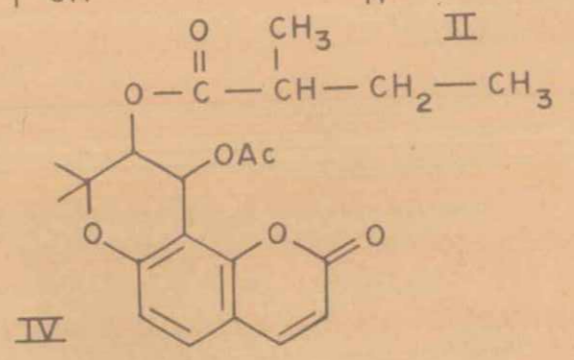
I



II

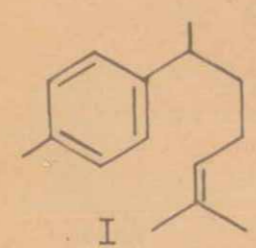


III

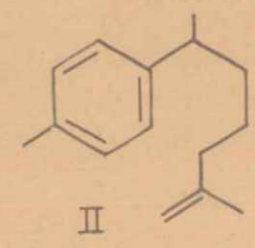


IV

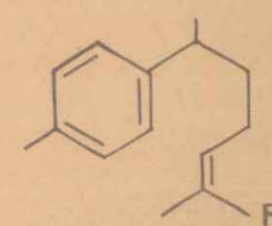
TURMERIC OIL (P. 53)



I



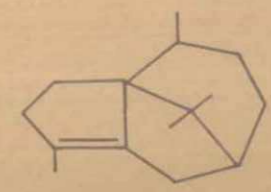
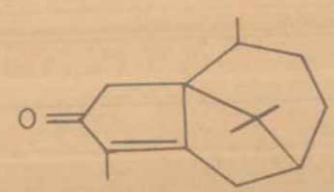
II



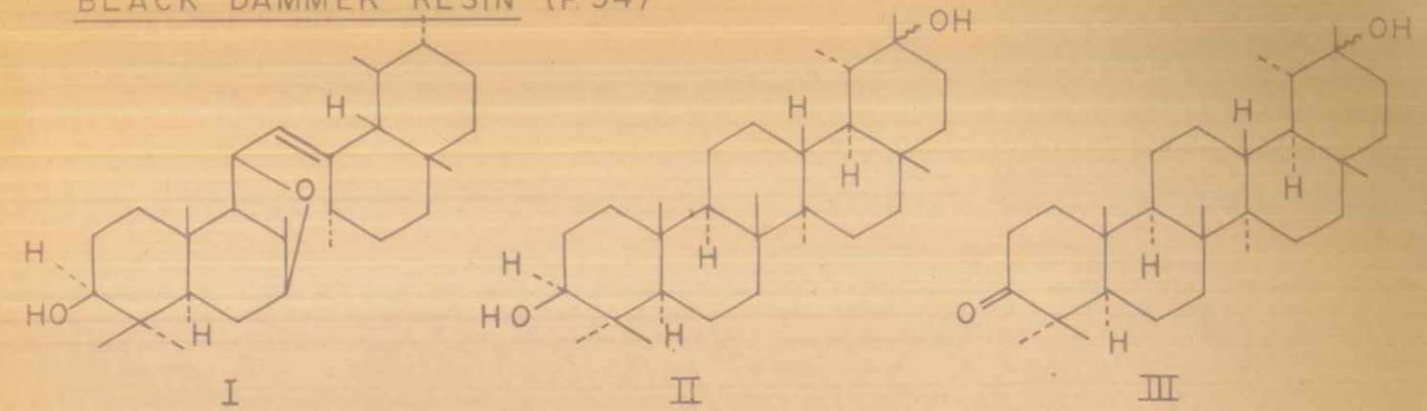
III, R = -CO₂H

IV, R = -CHO

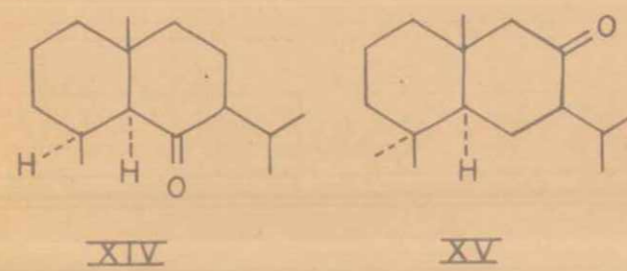
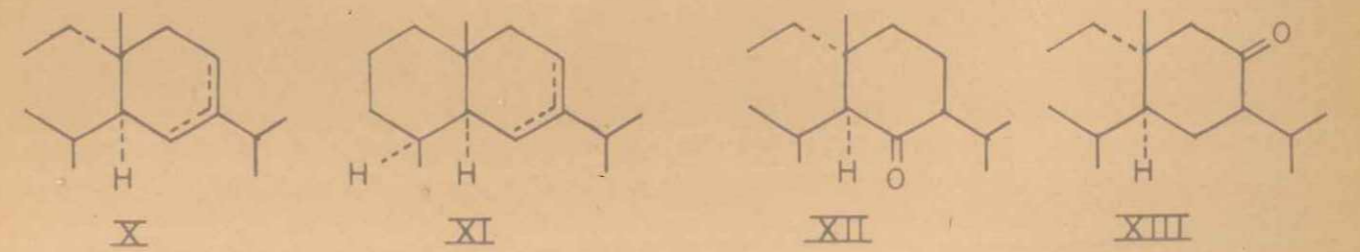
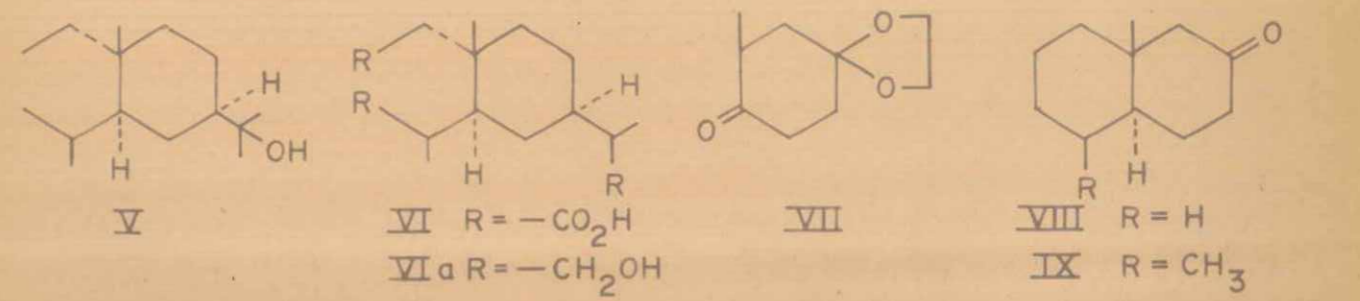
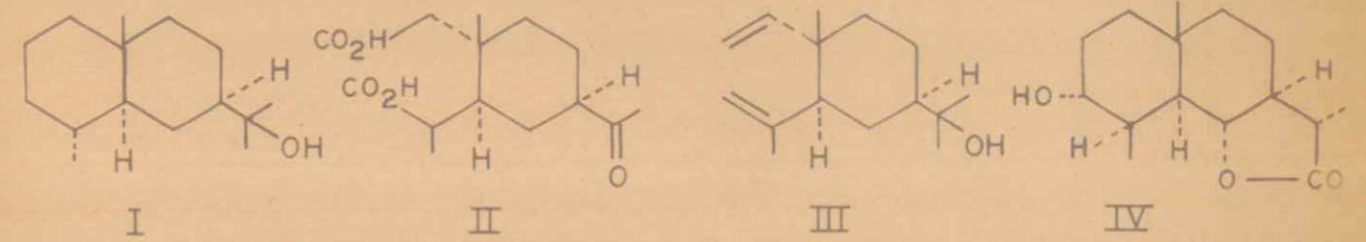
CYPERUS SCARIOSUS (P. 54)



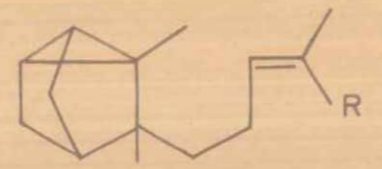
BLACK DAMMER RESIN (P. 54)



COMPOUNDS RELATED TO SELINANE AND ELEMENE (P. 54)

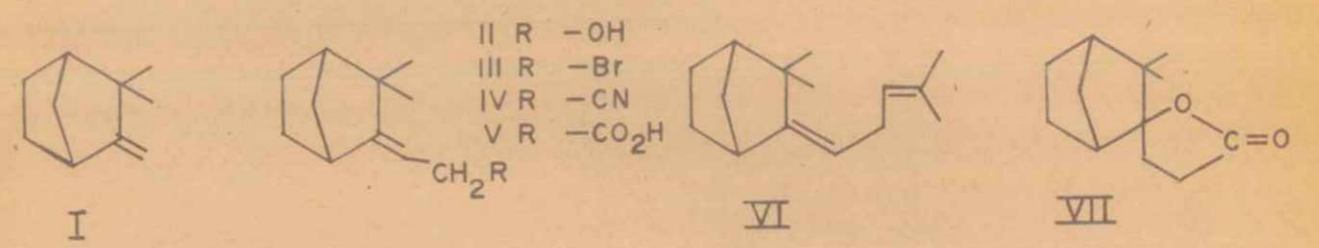


TRANSFORMATION PRODUCTS OF TRICYCLOEKASANTALIC ACID (P.55)



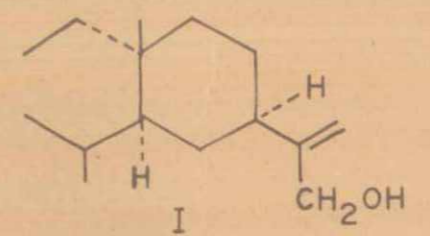
I, R = CH₃ II, R = -CO₂H III, R = -CH₂OH

SANTALENE - LONGIFOLENE SERIES (P.56)

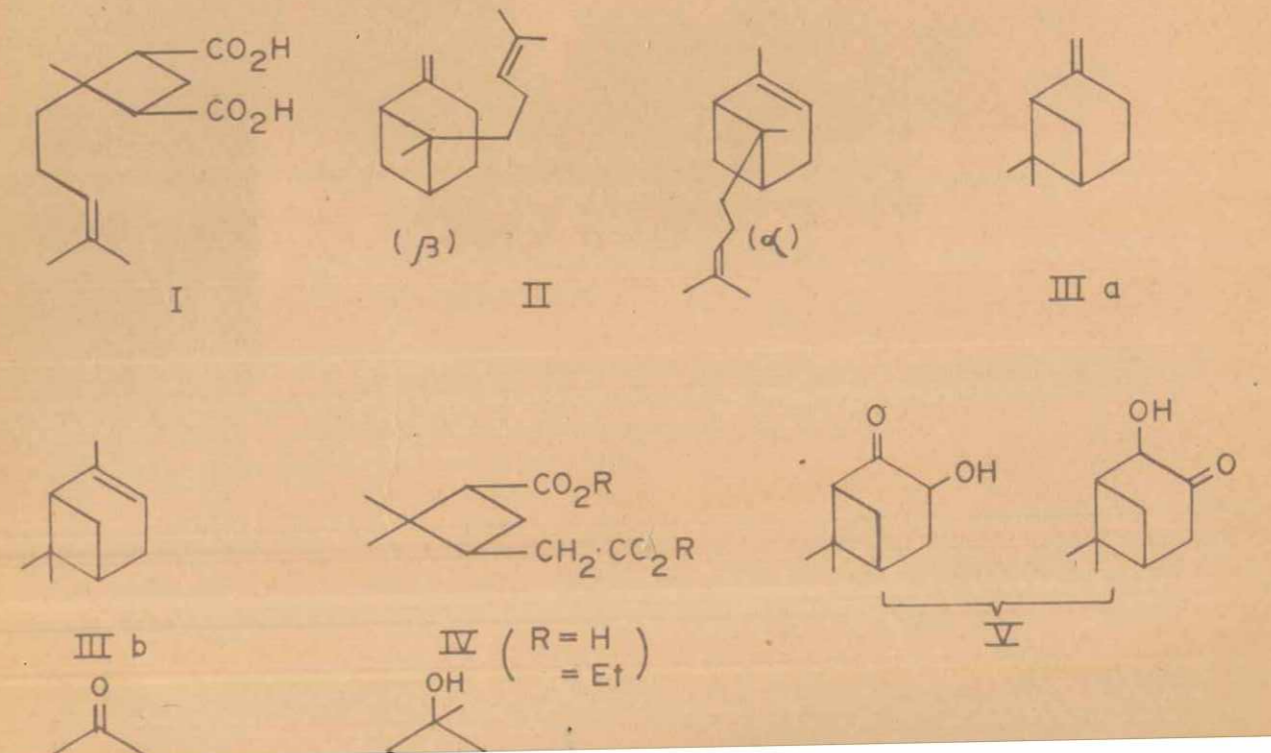


II R -OH
III R -Br
IV R -CN
V R -CO₂H

SELENIUM DIOXIDE OXIDATION OF TERPENES (P.56)



BERGAMOTENES (P.56)



11. Oxidation of alkyl side-chains in aromatic compounds
(1964) (Dr. Sukh Dev)

The liquid phase, catalytic oxidation of m-xylene has been studied in detail and a complete analysis of the reaction product has been carried out. Besides m-toluic acid, other components so far characterized are isophthalic acid, m-tolualdehyde, m-tolylearbiny l butyrate.

12. Apomorphine (1965)

Various methods available in the literature for the production of apomorphine from morphine have been examined but have been found to be unsatisfactory. A systematic investigation of this acid-catalysed rearrangement will now be carried out.

13. Conversion of thebaine ^{to} codeine (1965)

The first step involving the conversion of the thebaine into codenone has been investigated. A suitable TLC system for the analysis of thebaine and codenone mixture has been worked out.

14. Modification of cyclolaudenol (1965)

Step-wise degradation of cyclolaudenol (I) to the nor-compounds (II) has been standardized and its further conversion into (III) is being studied. (See figs. I to III on p.58).

B) Synthetic Dyes (Dr. K. Venkataraman) (1962)

During the six-monthly period under report, progress has been made in the following directions:

1. Preliminary results on the application of NMR spectra to the study of azophenol-quinonehydrazine tautomerism, which is of general interest in connection with the structures of azo and azoic dyes, have been outlined in a recent paper (Chimia, 19, 1965, 213). This work is being extended and continued.

2. By condensing cyanuric chloride with 1, 2 or 3 molecules of hydrazine and interaction of the products with ethyl

prepared and the preparation of azo and azoic dyes derived from them is being studied. Azo dyes derived from pyrazolone are mainly acid colours characterized by high light fastness, but pyrazolones have found little use as coupling components for azoic dyes and azo dyes for cotton. More complex dyes in which the second or third chlorine atom in cyanuric chloride is condensed with a chromophoric group are also being prepared.

By the action of acetic anhydride and pyridine on 1-hydrazino-s-triazine carrying dimethylamino and similar groups in the 3, 5-positions, triazolotriazines have been prepared and their preparation and reactions are under study.

3. As part of a general study of azoic dyes, the structures of new azoic coupling components are being examined. Methods are being developed for determining the structures of commercial reactive dyes.

4. In connection with the constitution of lac pigments, some of which have been shown to be derivatives of 2-phenylanthraquinone, methods for the synthesis of 2-arylanthraquinone are under investigation. An old IG patent describes the arylation of 1,5-diamino-4,8-dihydroxyanthraquinone-2,6-disulphonic acid in presence of sulphuric and boric acids and a possible mechanism has been suggested. The arylation of 1-hydroxy-4-nitroanthraquinone under similar conditions is being studied, and while our work was in progress, several patents have appeared on a similar reaction carried out on 1,5-dihydroxy-4,8-dinitroanthraquinone. The products are useful intermediates for acid-mordant dyes, reactive dyes, and disperse dyes for polyester fibres. The work includes a study of the reaction mechanism.

5. Work outlined in the last report on the reductive methylation and acetylation of anthraquinonoid vat dyes,

solubilized vat colours has been developed and is being used for the isolation of the parent vat dyes in pure form. Work on steric effects in the light absorption of violanthrone derivatives has been continued and a paper will be shortly communicated to the Indian Journal of Chemistry.

C) Carbohydrates (Dr.J.L. Bose)

1. Cyclic acetals of monosaccharides (1962)

This work was taken up with a view to improve the yields of 2,3;4,6,6-di-O-isopropylidene- α -L-sorbifuranose (DAS) a key intermediate in the synthesis of L-ascorbic acid and to study the mechanism of acetonation of sorbose and other monosaccharides to have a better understanding of the formation of DAS and other cyclic sugar acetonides.

The work carried out so far in this laboratory demonstrated clearly that DAS is formed via 1,2-O-isopropylidene- α -L-sorbopyranose (1,2-MAS) which supported the mechanism of formation of DAS proposed recently by the Japanese workers in this field. The equilibrium $\text{DAS} \rightleftharpoons 2,3\text{-MAS}$ (2,3-O-isopropylidene- α -L-sorbifuranose) has been studied in details under the conditions of acid-catalyzed reaction, however, optimization beyond an yield of 78-80% of DAS could not be attained so far. Literature or patent claims of more than 90% yield of DAS could not be substantiated. A detailed study is also made of copper sulphate catalyzed acetonation of 2,3-MAS and it is confirmed that its quantitative conversion to DAS is possible.

A detailed study is carried out on the copper sulphate acetonation of sorbose for a better understanding of a claim that over 90% ^{yield} of DAS can be obtained by copper sulphate acetonations, if carried out with traces of sulphuric acid. These studies have revealed that the copper sulphate catalyzed reaction produced in addition to DAS and 1,2-MAS, two more di-O-isopropylidene-L-sorboses and one mono-O-isopropylidene-L-sorbose (MAS-1). The formation of the latter 3 derivatives of L-sorbose in this reaction

been isolated in the pure state by preparative layer chromatography. The structure of the new MAS-1 has been established as 1,2-O-isopropylidene- α -L-sorbofuranose. DAS-1 has been found to be identical with 1,2:4,6-di-O-isopropylidene α -L-sorbofuranose recently obtained by the Japanese workers by ketal interchange reaction of L-sorbose with 1,1 diethoxypropane.

It is proposed to examine the validity of the claim of high yield of DAS by copper sulphate catalyzed acetonation of L-sorbose in which small amounts of sulphuric acid is also used. It is also proposed to establish the structure of DAS-2.

2. Preparation of some carbohydrate derivatives of interest to commerce and research laboratories (1965)

This work was undertaken with a view to prepare some useful carbohydrate derivatives required by commerce and research laboratories for various purposes. The method of preparation of D-glucosamine hydrochloride starting from crab and prawn shells was standardized and small quantities of the product were supplied to B.J. Medical College, Poona.

The method of preparation of diethylaminoethyl cellulose of required degree of substitution is standardized and some of the material is prepared and supplied to FCP.

Standardization of the methods of preparation of 2-deoxyribose, D-arabinose and acetobromoglucose have been taken up and preparation of other important carbohydrate derivatives will be taken up in near future.

D) Synthetic Drugs (Dr.J.L. Bose)

1. 4-(o-Hydroxyphenol)-cinnolines (1964)

A new synthetic route has been developed for the preparation of hitherto unknown 4-(o-hydroxyphenyl)-cinnolines. These products are of possible therapeutical value.

The steric effect of various substituents on the two aromatic rings of 2,3,4-triketochroman-3-arylhydrazone intermediates on the cyclization are studied and cyclizations are

Research Institute for screening and the results are awaited.

2. Meerwein arylation of 4-hydroxycoumarins (1964)

The object of this study is to prepare 3-aryl-4-hydroxycoumarins from appropriate 4-hydroxycoumarins and study their possible anticoagulant and oestrogenic properties.

In the course of the work on standardization of the reaction conditions some side reactions are observed which led to the preparation of hitherto unknown o-hydroxyphenyl glyoxal monoxime monohydrates. These o-hydroxyphenylglyoxal monoxime monohydrates have been transformed to coumarandione derivatives under various conditions.

Attempts are now being made to improve the yields of 3-phenyl-4-hydroxycoumarins by blocking the hydroxyl group in the 4-position prior to the arylation reaction.

PHYSICAL ORGANIC CHEMISTRY

Long Range Spin-spin Coupling in the Study of Aromatic Electrons (1963) (Dr.P.M. Nair)

It has been shown that the magnitude of the first order coupling constants $J_{CH_3-H_{Ar}}$, for a number of closely related methyl substituted aromatic compounds varies linearly with the mobile bond order between the carbon atoms involved.

4-Methylbenzocyclobutene has been prepared and its NMR spectrum compared with that of 5-methyl indane. The NMR data suggest that the effect of the strain introduced by the 4-membered ring on the aromatic ring is not of the same type as in the case of benzocyclopentane (indane). The data are under further consideration.

The studies on benzocycloalkenes are being extended to their hetero analogues.

In an attempt to study changes in benzene ring geometry produced by strongly interacting substituent groups the NMR spectra of the esters of the three toluic acids and the isomeric nitrotoluenes have been examined. The idea is to use the weakly interacting methyl group as a sensing element to determine the changes brought about by the carboxyl and nitro groups. The methyl band widths observed suggested that 3-4 and 4-5 bonds of benzoic acid are shorter than the 2-3 and 5-6 bonds. Although these results cannot be rationalized in terms of any molecular orbital treatment of benzoic acid so far given, they are consistent with X-ray crystallographic data. An effect of the same type as for the carboxyl group is probably produced by the nitro group also; although to a smaller extent. The problem is under further study.

Carbonium Ions

Although carbonium ions have been postulated as intermediates in numerous reactions direct observations of these entities and their properties have been made only recently. A number of reports have already appeared on the subject; but they have not helped in finding a satisfactory answer to certain fundamental questions regarding the nature of carbonium ions in solution.

The NMR spectra of a number of carbonium ions have been recorded in an effort to get a clearer understanding of their nature. The data gathered have proved to be very interesting and their significance is being considered.

BIOCHEMISTRY

A) Microbiology (Dr.V. Jagannathan)

The main objectives of work in this field are (a) maintenance of the National Collection of Industrial Microorganisms, (b) study of new fermentations, and (c) fundamental studies on

1. National Collection of Industrial Microorganisms (Perm.)

The culture collection consists of about 1200 non-pathogenic yeasts, bacteria and fungi which are of importance in research and industry. Cultures are supplied free of charge on request to scientific institutions and industry.

Routine maintenance, subculturing and testing of microorganisms for biochemical performance are carried out. During the period, 355 cultures were distributed on request to industrial concerns and research institutions.

2. Microbiological oxidation of hydrocarbons (1965)

Several microorganisms which can oxidize hydrocarbons such as kerosene have been reported in recent years. Exploratory work on the isolation of cultures which can grow on kerosene is undertaken. Three cultures are obtained which can grow rapidly on kerosene and the possibility of utilizing these cultures for producing industrially useful chemicals such as amino acids is being investigated.

3. Bacterial diastase (1960)

Fermentation trials are carried out to test stock cultures and tests are undertaken on different antifoam agents and filter aids at the request of the firm to which the process is leased. Assistance is given to a representative of the firm by demonstrating the fermentation and isolation and testing of the enzyme.

4. Growth of plant cells (1959)

The objective is to study plant cells grown in vitro in order to investigate their growth and metabolism and to examine the formation of useful plant products.

The requirements for the continuous growth in vitro of cells from several different plants (opium, cholai, digitalis, etc.) are determined in previous years. Twenty five plant cell cultures are being maintained at present of which some ~~ix~~ are isolated and established as viable in vitro cultures for the first time in this

(a) to determine the requirements for rapid growth of plant cells, especially of cholai bean cells, since the slow rate of growth of plant cells limits their usefulness for metabolic and enzyme studies, and (b) to study the growth of monocotyledonous cells and other plant tissues which have hitherto been investigated only to a limited extent though they are of very great agricultural importance.

Sub-culture of maize callus culture tissue isolated in this laboratory is continued in order to determine its viability on maintenance indefinitely in vitro. The studies on the effect of other growth constituents such as different sugars and mineral salts on the growth of the culture are being continued. In all cases a mixture of root and callus tissue is obtained. Attempts to obtain growth from single cells and the nutrient requirements for these are being investigated both for maize and for other tissues. Several compounds similar to diphenylurea are being synthesized and tested for their effect on maize growth and viability.

Strains of normal and tumour tissue from different sources are being obtained and a comparative study of the effect of specific growth inhibitors and anti-tumour compounds on the normal and the tumour strains of the same tissue is in progress. No significant difference in the lactic dehydrogenase and hexokinase of the two tissues is observed.

700 gms. of parthenocissus crown gall are grown and the lipids are isolated. Estimations of ubiquinone and determination of the nature of ubiquinone present in the normal and the tumour tissues are in progress. Studies on the ubiquinone content of other microorganisms are also continued. The presence of ubiquinone in S. griseus is noted. In A. niger no ubiquinone is detected in the spores whereas there is a rapid increase in the ubiquinone content on germination and especially on growth in submerged conditions.

In order to clarify the differences observed in the growth of plant tissue cultures on different sugars a study of the hexokinase and phosphofructokinase of different plant materials is undertaken. Wheat bran is particularly found to be rich in hexokinase and the isolation and properties of this enzyme are being investigated.

B) Enzymes (Dr.V. Jagannathan)

1. Hexokinase (1963)

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 work on the purification of this enzyme, which plays an important role in carbohydrate metabolism, is in progress.

On DEAE cellulose chromatography and ammonium sulphate fractionation in the presence of stabilisers brain hexokinase is purified to a specific activity of about 50 units per milligram protein. The enzyme at this level of purity is found to be 80 to 85 per cent pure by ultracentrifugal studies. The kinetics and properties of the enzyme are being studied.

2. Phytase (1964)

The objective is to study a new bacterial enzyme which specifically hydrolyses inositol hexaphosphate. The purification of the enzyme and the study of its properties and specificity were undertaken.

The partially purified enzyme is used for the isolation of the product of phytate hydrolysis and for determining its structure. Approximately half the total phytate phosphorus is found to be hydrolysed and the resulting product shows no reaction with periodate indicating the absence of vicinal hydroxyl groups. Chromatographic methods for the preparation and purification of phytate and the reaction product are worked out and a large scale isolation of the product is in progress.

3. Acetylcholinesterase (1964)

This enzyme which plays an important role in the metabolism of brain and nerve has been obtained in soluble form and purified to a considerable extent only from the electric organs of some fish. A new method has been worked out for the preparation of soluble acetylcholinesterase from ox brain. The enzyme has now been purified about 40-fold by calcium phosphate gel adsorption and DEAE cellulose chromatography. Further work on the purification of the enzyme is in progress.

4. Brain DP Nase (1965)

This enzyme which splits DPN and TPN at the nicotinamideribose link has been obtained for the first time in soluble form from beef brain. Work on the isolation of this enzyme is being continued.

5. α -Amino acid acylases (1963) (Dr.C. Sivaraman)

Enzymes of the class α -amino acid acylases have found extensive application in recent years in the preparation of optically pure L- and D-amino acids as they specifically hydrolyse N-acylated derivatives of the L-isomer and the subsequent separation of the free amino acid from the unhydrolysed derivative can be carried out with relative ease. The purification and properties of fungal acylases, which have not been investigated as extensively as the mammalian enzymes, are therefore undertaken.

In earlier work carried out in this laboratory, a relatively crude preparation of acylase from Aspergillus flavus-oryzae has been shown to differ from the mammalian enzymes in its substrate specificity and metal requirements. The enzyme had also been purified extensively by solvent and salt fractionations and chromatography on cellulose-calcium phosphate and DEAE-cellulose columns. Some difficulties are encountered in obtaining active preparations from cultures of the fungus.

The original levels of enzyme activity could be reproduced with fresh soil cultures of Aspergillus flavus-oryzae. The purified enzyme has a broad pH optimum between the range 7.0 to 8.5; for both acetyl-alanine and acetyl-tryptophane. The purified enzyme is partially inactivated by

reactivated by Zn^{2+} and not by Fe^{2+} , Fe^{3+} , Co^{2+} and Mn^{2+} . The relative rates of hydrolyses of formyl, acetyl and chloroacetyl derivatives of alanine, tryptophane, phenylalanine and aspartic acid by the purified enzyme are determined. Interesting differences are observed between the susceptibilities of the different substrates towards the fungal enzyme preparation and the enzymes from mammalian sources.

The investigation would be completed in this quarter after some studies on the kinetics of the hydrolysis.

C) Inorganic Nitrogen Metabolism (1964) (Dr.J.C. Sadana)

The objective of this investigation is to elucidate the mechanism of nitrate and nitrite utilization by the luminous bacterium Photobacterium fischeri.

Earlier studies resulted in the characterization of nitrate reductase from P.fischeri. The formation of nitrite reductase by P.fischeri was demonstrated for the first time in this laboratory. This is contradictory to the conclusion reported by McElroy et.al. that P.fischeri can form inducible nitrate reductase but no nitrite reductase. The procedure for purification of nitrite reductase from P.fischeri was standardized and the sequence of electron transport for nitrite reduction worked out.

Conditions for the growth of P.fischeri with a view to obtaining high yields of nitrite reductase as well as enzyme with a higher starting specific activity are worked out. Nitrite reductase formation decreases with increasing oxygen tension and is absent in cells grown in nitrate-free medium. The purified enzyme is 20 times more active than the most active preparation reported so far. The pH optimum for nitrite reduction is 7.4 and the Michaelis constant for the enzyme-nitrite complex is 4.1×10^{-5} M. Cyanide (10^{-3} M) and carbon monoxide (1 atm, in the dark) completely inhibited the enzyme. Inhibition by carbon monoxide is reversed by light. The purified enzyme shows absorption bands at 280, 520 and 550 and a Soret peak at 419 m μ in the reduced state. The spectrum of the reduced enzyme reverted to that of the oxidized state on addition of nitrite.

The data obtained strongly suggests that nitrite reductase from *P. fischeri* is in haem-containing protein.

3 x crystallized lysozyme and 2 x crystallized α -ketoglutaric acid are prepared for FCP.

Further studies on the nitrate metabolism by *P. fischeri* will be continued. In order to characterize the enzyme nitrite reductase conclusively, it is intended to collect sufficient quantities of the purified enzyme to test for its homogeneity.

D) Microbiological Transformations of Terpenes
(1959) (Dr. P.K. Bhattacharyya)

This work of fundamental interest is undertaken with a view to (a) converting easily available terpenic hydrocarbons into oxygenated products of potential interest to perfumery industry with the aid of microorganisms and (b) elucidating the biochemical mechanisms underlying these transformations.

Earlier studies had indicated that fungi and bacteria can bring about in mono- and sesquiterpenic hydrocarbons as well as in alicyclic model substrate, chemical changes such as hydroxylation, hydration and oxygenation on double bonds with or without rearrangements, oxidation of functional groups and carbon-carbon bond cleavage including the rupture of carbocyclic rings.

1. Fungal transformations - Mechanism of fungal hydroxylations

A strain of *Aspergillus niger* (NCIM 612) selected on the basis of its versatility in metabolising a variety of terpenic hydrocarbons is found to carry out stereospecific allylic hydroxylations in a large number of substrates giving rise to optically active products. However, in two cases, viz. in the formation of 2-hydroxy-1-methyl-3-cyclohexene and α -tetralol from the parent hydrocarbons, 1-methyl-3-cyclohexene and tetralin respectively, complete racemisation is encountered. The preservation of stereospecificity in most cases as well as its failure in the other can be explained by a "hot" carbonium ion mechanism analogous to the one involved in the deamination of optically active primary amines by nitrous acid.

Assuming that a "hot" carbonium ion is involved in the fungal hydroxylation and taking into account the literature data available on biological hydroxylation of steroids and aromatic compounds, it can be predicted that on hydroxylations in which stereospecificity is preserved the hydroxyl oxygen is likely to derive almost entirely from atmosphere, whereas in the racemic metabolites these hydroxyls are likely to be formed to a great extent from the aqueous medium. Studies are in progress to verify these predictions.

2. Bacterial transformations

Synthetic studies to determine the structure and stereochemistry of some products of fermentation of limonene and the pinenes by a soil pseudomonad (PL strain).

The structure and stereochemistry of some of the products derived from limonene (1) by fermentation with pseudomonad (hereafter designated as the PL strain) are established by their chemical synthesis. (+)Dihydrocarvone (3), (+)8-p-menthene-1,2-trans-diol (4), 8-p-menthene-1-ol-2-one (5) and (-) carvone (6) are synthesized from limonene - 1,2-oxide (2). (See figs. 1 to 6 on p.78).

It is thus established that the stereochemistry of the fermentation products, 3,4,5, is identical with that of products derived chemically by an epoxydation at 1,2 double bond in limonene (1) and that probably compound 2 is produced during fermentation. (+) Carvone (7), however, is probably derived from (+) carveol formed by a true allylic oxidation process in the microbial system and not through the epoxide (2) which should give rise to the antipodal ketone (6).

The structures of β -isopropyl-pimelic acid (11) a fermentation product from α -pinene (8), β -pinene (9) and 1-p-menthene (10) and of β -isopropenyl pimelic acid (12) from limonene (1) [as (12) gives (11) on catalytic reduction] are established by the total synthesis of (11) by the following

route. The absolute configuration of compound (11) (as well as that of compound 12) has been established by another synthesis of 11 from (+) 1-*p*-menthene: (See figs. 2 to 12 on p.78).

The specific rotation of the synthetic product $[(\alpha)_D^{25}]$ is identical with that of the bacterial metabolite (11). This synthesis also provides unequivocal proof for the earlier contention that an inversion occurs at position 4 in β -pinene before the formation of compound 11 through fermentation.

3. Fermentation of 1-*p*-menthene

It was reported earlier that a major pathway of degradation of α and β -pinenes in the PL strain involved *p*-menthenoid intermediates with a saturated isopropyl side-chain eventually leading to the saturated β -isopropyl pimelic acid.

It is thus considered necessary to study the fermentation of 1-*p*-menthene by the PL strain. Among the fermentation products tetrahydrocarvone (13), dihydrocarveol (14), *p*-menth-1-ol (15), phellandric acid (16), 2-hydroxy-*p*-mentha-7-oic acid (17) and β -isopropyl pimelic acid (11) have been identified. The formation of compounds (16) and (18) in the fermentation of α and β pinenes (8,9) have been demonstrated earlier.

The stereochemistry of compounds (13), (14) and (15) is under investigation. (See figs.13 to 17 on p.79).

Fermentation of *p*-cymene ()

Among the fermentation products of *p*-cymene (18) two new compounds (19 and 22) have been identified.

Compound (22) is likely to be an artifact derived from compound (21) during methylation with diazomethane.

Adaptive enzyme studies have clearly indicated that in the degradation *p*-cymene (18) cumic acid (20) proceeds to the dihydroxy acid (21) in a single stage by a dioxygenation reaction. Neither of the mono hydroxy acids (23) or (24) serves as a growth

grown cells. The dihydroxy acid (25) without the isopropyl side chain, on the other hand, is freely metabolised by these cells with or without chloramphenicol, although the exact relationship of (25) with the pathway of *p*-cymene degradation remains to be elucidated. (See figs.18 to 25 on p.79).

5. Perillyl alcohol dehydrogenase

The substrate specificity of a NAD-linked dehydrogenase obtained from cell-free sonicates of the PL strain has been studied with a large number of substrates structurally related to perillyl alcohol, and cumyl alcohol. The following structural features appear to be necessary for activity: (a) a primary alcoholic group allylic to an endocyclic double bond in a six-membered ring; (b) absence of any substituent ortho to the primary alcoholic group. Meta substitution slightly reduces the activity whereas the presence of a short alkyl side chain in the para-position enhances the activity.

A comparison of relative activities of this enzyme from PL strain grown on different substrates such as limonene α -pinene, β -pinene, *p*-cymene and glucose on four different reference substrates, perillyl alcohol, phellandrol, oleuropeyl alcohol and cumyl alcohol indicate that irrespective of the inducer the same enzyme is induced in each case. Glucose, however, represents the formation of the enzyme.

A further purification of the enzyme (18-25 fold on the sonicate level) has been achieved by chromatography of the Keileen and Hartree calcium phosphate gel eluate (described earlier) over a DEAE-cellulose column. The enzyme becomes unstable at this stage.

6. Fermentation of camphene

A pseudomonad (different from the PL strain), hereafter designated as the camphene-strain, has been isolated by enrichment culture techniques. Among the fermentation products

of camphene (26) by this strain camphinolone (27) isoborneol (28), camphor (29), 5-exohydroxycamphor (30), 2,5-diketocamphane (31) and 2,2,3-trimethyl-5-carboxymethylene-cyclopentenone (32) have been identified. It has been established that this strain converts camphene (26) to isoborneol (28) by a prototropic (Wagner Meerwein type) rearrangement. Isoborneol (28) is then dehydrogenated to camphor (29) which is then metabolised by, if not the same, a closely similar pathway followed by some camphor fermenting pseudomonads (C_1 and C_5 strains) under study at the University of Illinois. (See figs. 26 to 33 on p. 79).

The lactonising enzyme carrying out reaction (29) (30) which is first discovered at the University of Illinois in the C_1 and C_5 strains, has been demonstrated in the camphene strain.

The enzyme bringing about the prototropic rearrangement of camphene (26) to isoborneol (28) has been demonstrated in camphene grown cells under nitrogen as well as in cell-free extracts, of the camphene strain. The sonicates also contain more than one enzymic activity responsible for the NAD-specific dehydrogenation of isoborneol (28) to camphor (29).

A programme has been undertaken in collaboration with the University of Illinois group to study the similarities and differences of the camphene strain on one hand and the C_1 and C_5 strains on the other, with respect to various enzyme levels and the genetic make-up.

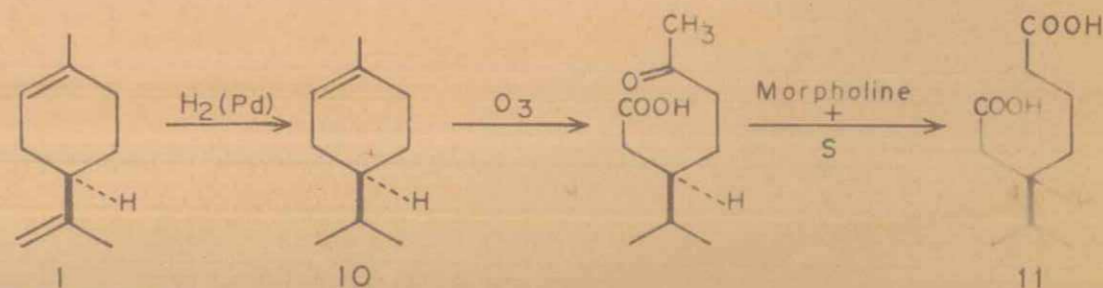
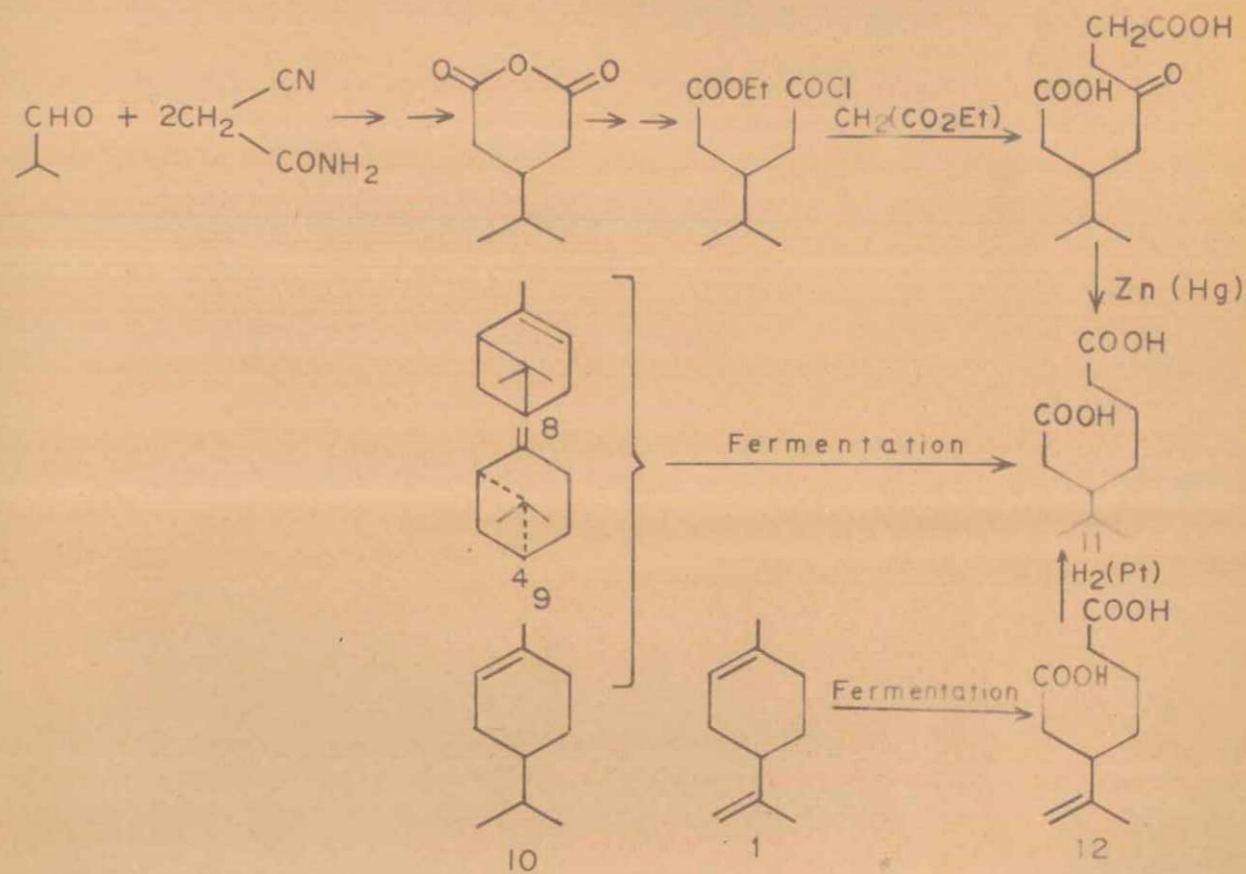
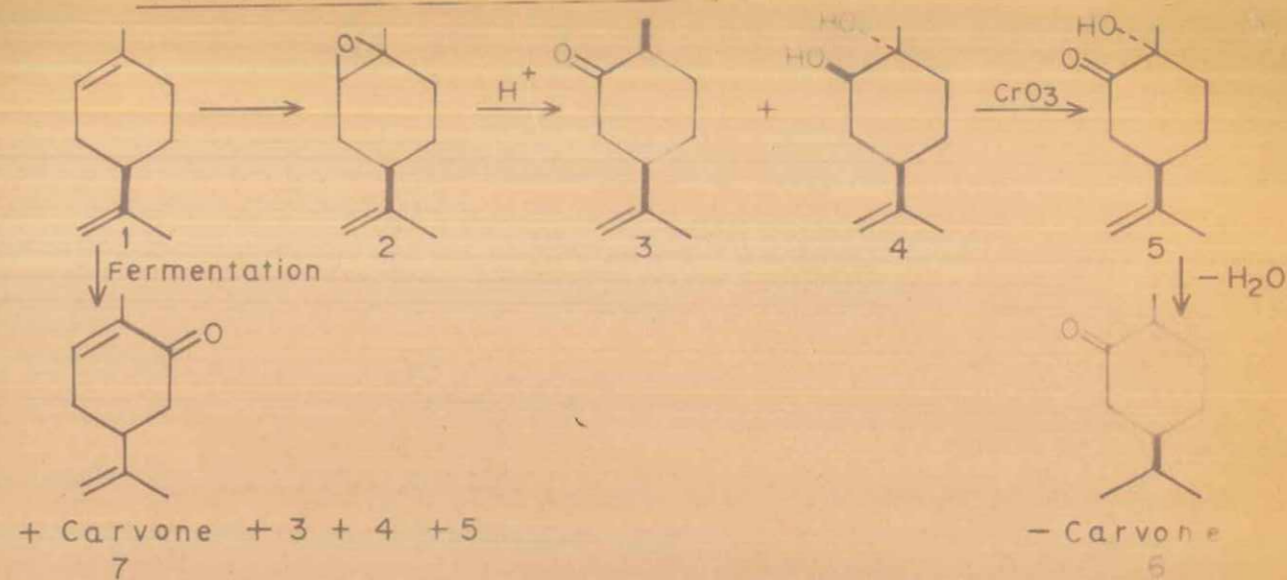
of camphene (26) by this strain camphinolone (27) isoborneol (28), camphor (29), 5-exohydroxycamphor (30), 2,5-diketocamphane (31) and 2,2,3-trimethyl-5-carboxymethylene-cyclopentenone (32) have been identified. It has been established that this strain converts camphene (26) to isoborneol (28) by a prototropic (Wagner Meerwein type) rearrangement. Isoborneol (28) is then dehydrogenated to camphor (29) which is then metabolised by, if not the same, a closely similar pathway followed by some camphor fermenting pseudomonads (C_1 and C_5 strains) under study at the University of Illinois. (See figs. 26 to 33 on p. 79).

The lactonising enzyme carrying out reaction (29) (30) which is first discovered at the University of Illinois in the C_1 and C_5 strains, has been demonstrated in the camphene strain.

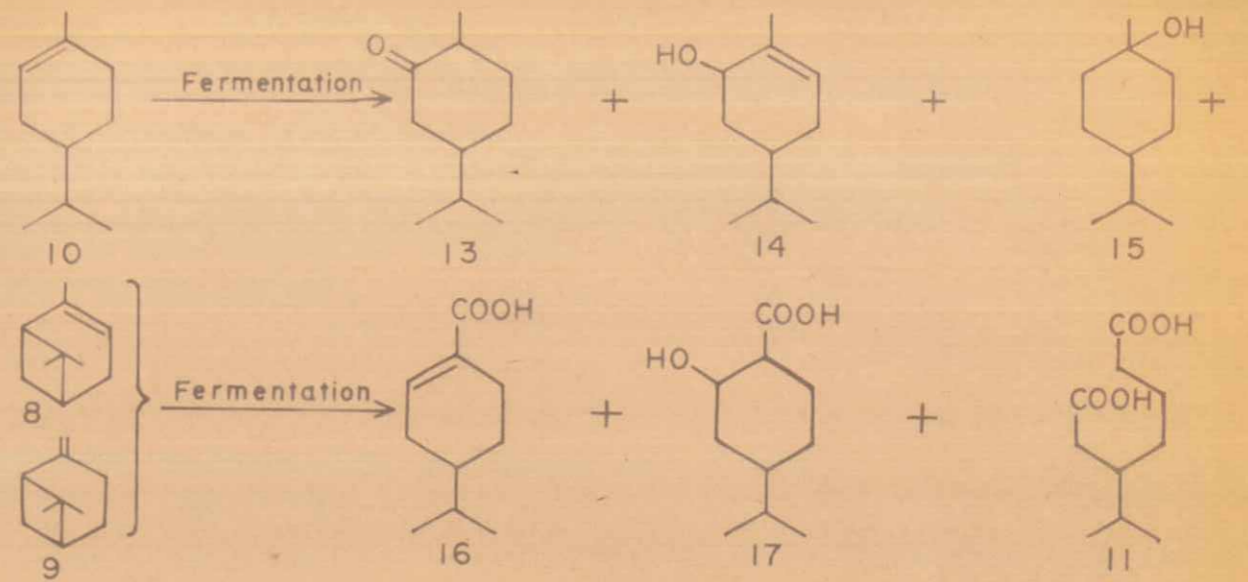
The enzyme bringing about the prototropic rearrangement of camphene (26) to isoborneol (28) has been demonstrated in camphene grown cells under nitrogen as well as in cell-free extracts, of the camphene strain. The sonicates also contain more than one enzymic activity responsible for the NAD-specific dehydrogenation of isoborneol (28) to camphor (29).

A programme has been undertaken in collaboration with the University of Illinois group to study the similarities and differences of the camphene strain on one hand and the C_1 and C_5 strains on the other, with respect to various enzyme levels and the genetic make-up.

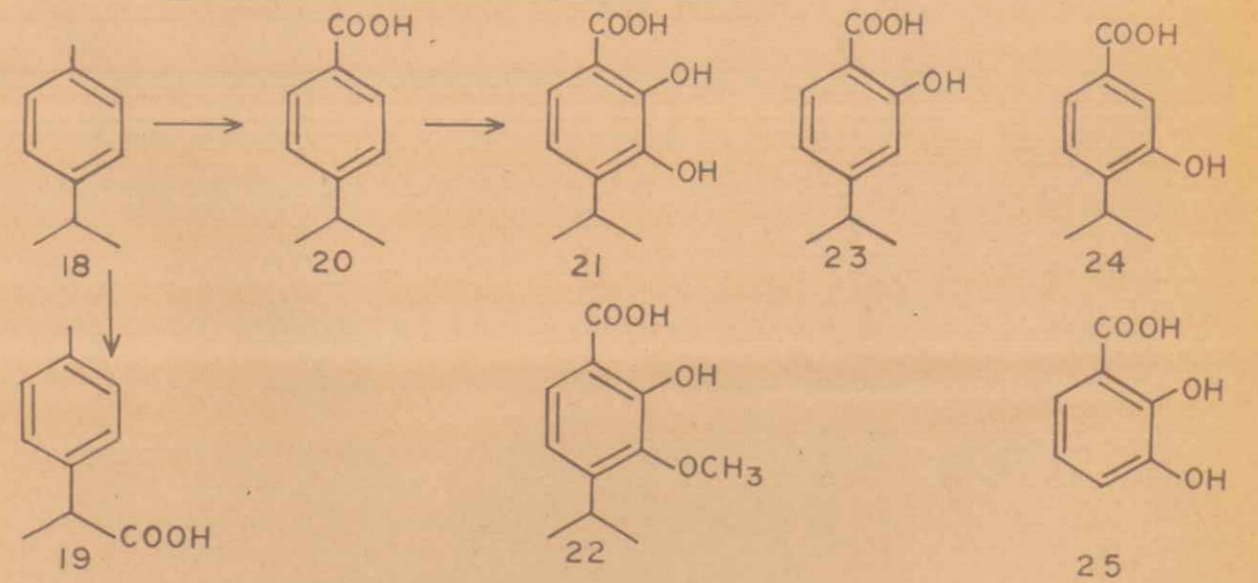
Bacterial transformation (P. 74 & 75)



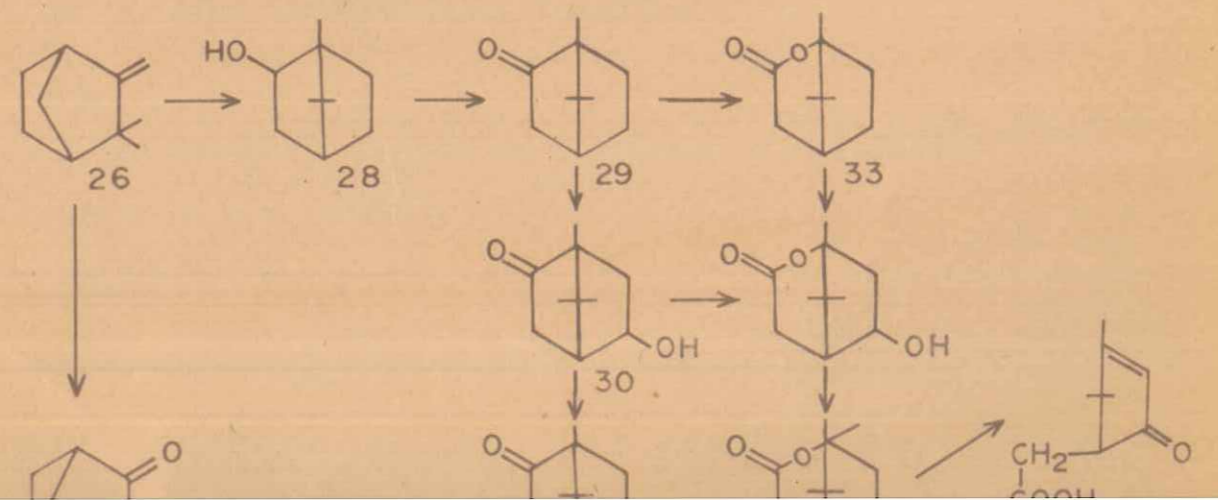
FERMENTATION OF l-p-menthene (P. 75)



FERMENTATION OF p-cymene (P. 75 & 76)



FERMENTATION OF camphene (P. 77)



A) Physicochemical Studies (Dr.S.L. Kapur)1. Solution properties of polymers (1956)

The study is directed to correlate the structure of polymers and copolymers with their solution behaviour. The applicability of new single parameter method of molecular weight determination is being studied for different polymeric materials.

In examining the applicability of the single parameter method of molecular weight determination of polymers from solution viscosities, the studies have been extended to randomly branched polyvinyl acetates. The ordinate $[\eta]_R$ at the common point of intersection of the $\ln \eta_r/C$ vs. C plots in different solvents correlates with the square-root of the viscosity-average molecular weight as in the earlier cases of polystyrene, polymethyl acrylate and linear polyvinyl acetate. The value of $[\eta]_R$ are higher than the intrinsic viscosities in ethyl n-butyl ketone at 29° (a theta solvent) as in the case of linear polyvinyl acetate due to 'specific solvent effects' on the unperturbed dimensions. It has also been demonstrated that η_R gives a better estimate of branching on polymers than intrinsic viscosities in good or bad solvents.

Solutions of fractions of p-chlorostyrene and methyl methacrylate copolymer obtained at the azeotropic composition have also been examined for the presence of 'specific solvent effects' on the unperturbed dimensions. Results obtained indicate that such effects are absent to within experimental error. The solution behaviour of poly p-chlorostyrene fractions is being examined by osmotic pressure, light-scattering and viscosity methods to correlate the effect of individual co-monomers on the spatial extension of the copolymer.

2. Stereospecific polymerization - Polymerization of styrene and isoprene (1960)

Studies of kinetics of polymerization of styrene with different Ziegler type catalyst systems is being studied.

In continuation of kinetics studies with different Ziegler type catalyst systems, polymerization of styrene with

concentrations for the first catalyst system. In the second system, however, the rate of polymerization varies linearly with monomer concentration and bimolecularly with catalyst concentration. The activation energy is 14.5 Kcal/mole for the first system and 11.5 Kcal/mole for the second system.

At present work is in progress with the catalyst $ZrCl_3-Al(i)Bu_3$. $ZrCl_3$ has been prepared by the reaction of 3 moles $ZrCl_4$ with 1 mole of aluminium triethyl in decalin at 150° for 2 to 3 hours. The product is separated and purified by subliming out $ZrCl_4$. The rate of polymerization of styrene is maximum at a ratio of 2 for Al/Zr and at the same ratio the rate of polymerization is constant for more than 2 hours.

In order to understand the nature of the complex formed in the catalyst system $VoCl_3-Al(i)Bu_3$, the valences of vanadium in the combination of $VoCl_3$ with $AlEt_3$, $Al(i)Bu_3$, $AlEt_2Br$, $Sn(C_3H_7)_4$ and LiC_5H_{11} have been determined by potentiometric titration of redox system of acidic solution of catalyst complex against ceric sulphate and potassium permanganate under inert atmosphere at 70° .

3. Telomerisation (1964)

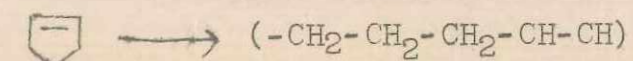
With a view to produce nylon-7 polymer indigenously, telomerisation studies were undertaken with the help of a Russian expert.

This work is continued to investigate the effects of different initiators like phthalloyl dibenzyl peroxide and nitroso compounds. It is observed that phthalloyl dibenzoyl peroxide is an effective catalyst for the telomerisation of ethylene with carbon tetrachloride. The required type of telomer formed at 105° and 90 to 100 at ms. Due to lack of staff and due to other priority projects, this work is temporarily interrupted.

4. Polymerization of turpentine fractions (1965)

It is known fact that turpentine fractions like Δ^3 -pinene

initiators like boron trifluoride to low molecular weight products. Recently Ziegler type catalysts have been used to polymerize turpentine oil fractions to low molecular weight solid polymers. Ziegler type catalysts have also been used to polymerize cyclopentene leading to open chain compounds with elastomeric properties, as shown below:



On the same lines exploratory work for the polymerization of turpentine oil as such and separate fractions of Δ^3 carene (Δ^3 and Δ^4 carene fractions are present in Indian turpentine oil) with Ziegler type catalyst systems, such as, $TiCl_4-AlEt_2Br$ and $VoCl_3-AlEt_3$ at 0° , has been started. A low molecular weight solid has been obtained from turpentine and a resinous polymer has been obtained from Δ^3 carene. Further work is continued to standardize the conditions, to improve the yield and to study the physical properties of the products.

B) Ion Exchange Materials

1. Study of cardanol formaldehyde polymerization (1962) Dr. K.P. Govindan

Besides studying the reaction of saligenin with styrene and maleic anhydride, 6-methylol derivative of tetrahydro cardanol has been reacted with the above compounds. The yield of chroman derivatives is higher with 6-methylol cardanol than saligenin. Further studies with 6-methylol etc. are in progress.

2. Styrene base ion-exchange resins with different cross-linking agents (1962) Dr. K.P. Govindan

a) Some more batches of the sulphonic acid type cation exchangers from styrene furfural reaction product were prepared and a 70 cm. bed of the resin was set up for evaluation of column characteristics. Besides this, the influence of temperature on the capacity of the resin and its rate of exchange have also been determined.

b) Different concentrations of chlorosulphonic acid were employed for sulphonating the polystyrene paraformaldehyde reaction product.

c) Preliminary investigations have been undertaken towards preparation of macroreticular ion-exchange resins employing newer polymerization techniques.

3. Styrene-DVB base cation exchange resin
(1960) (Dr. S.L. Kapur)

A series of experiments have been conducted to prepare a modified copolymer using different solvents as diluents and the process of polymerization has been standardized. The copolymer so prepared has been sulphonated in 750 gm/batch. The improved technique for washing the sulphonated copolymer with the help of a centrifuge/column, has led to a considerable improvement in the physical characteristics of the final resin. It is proposed to scale up this procedure so that problems associated with the washing of large quantities of the sulphonated copolymer are realized. Suitable equipment for this purpose is under fabrication. Samples of improved resin so prepared have been sent to a few parties for their expert evaluation.

4. Styrene-DVB base anion-exchange resins
(1961) (Dr. S.L. Kapur)

With a view to get the required standard capacity in the final resin, a few experiments to obtain the maximum degree of chloromethylation in the copolymer have been carried out. Using solvent-modified copolymer and copolymers of different degrees of cross-linkage, conditions for obtaining the final product (using trimethyl amine for amination) possessing required physical and chemical characteristics have been investigated. On the basis of these findings, experiments starting with 2 kg. of copolymer per batch are being planned. Repeated trials will

Systematic studies in the amination of chloromethylated copolymer using dimethyl-amino-ethanol have been carried out so as to raise the capacity of the final resin to the required value of 3.8 meq/gm. The use of increased period and temperature of reaction and larger concentration of the amine do not lead to any substantial increase in the capacity. The use of different swelling agents prior to amination is being examined.

5. Carboxylic cation exchangers from cold extracted CNSL
(1962) (Dr. K.P. Govindan)

1 kg. of the granular carboxylic cation exchanger has been prepared. Study of distribution of metal ions between the contacting solution at different pH values of the resin has been carried out to evaluate selectivity characteristics of the resin.

6. Melamine base anion-exchange resin (1960) (Dr. Govindan)

Large scale preparation of the improved melamine anion-exchange resin is being undertaken by the firm licensed to manufacture the resin. All work on preparation aspect in the laboratory has been discontinued. Application aspects are being studied.

7. CNSL anion exchanger (1961) (Dr. Govindan)

After confirming the performance of the resin as a weak base anion exchanger, the selectivity characteristics of this resin have been studied. It is found to have a high specific affinity for Cu^{++} ions at pH 5.0.

8. Electrodialysis with ion-exchange membranes
(1960) (Dr. Govindan)

Attempts are under way to scale up the electrodialysis cell. For this purpose the necessary equipment is being assembled along with preparation of large sizes ion-exchange membranes with the cooperation of M/s Swastik Rubber Products, Kirkee, Poona.

With the nine chambered cell, electro dialysis of sea water has been carried out at 100, 200, 300, 400 and 500 ma current. Increase in current density increased the percentage of salt reduced.

Results on diffusion effects reported earlier have been published. [J. Appl. Poly. Sci. 9, 2631 (1965) and Ind. J. Tech. 2, 361 (1964)]

9. Influence of high energy radiation on ion exchangers (1964) (Dr. Govindan)

Both dry and wet CNSL cation exchanger and melamine anion exchangers have been exposed to different doses of radiation. The progress of the effect has been obtained by determining loss in weight, moisture contents, loss in exchange capacity and appearance of acidity/alkalinity, in the washings. Further work is in progress with different types of ion-exchange materials.

C) Industrial Polymers (Dr.S.L. Kapur)

1. Polystyrene foams (1960)

Further experiments to standardize the polymerization steps are continued. The use of another grade of benzoyl peroxide as catalyst has led to the enhancement in the period of polymerization. The purity of the benzoyl peroxide and its effect on the molecular weight of the final product is under investigation. The large size kettle fabricated recently for scaling up the work, is not maintaining pressure over a period of 24 hours and it is proposed to put it into use after these defects are rectified.

2. Rigid sand filters (1960)

The pilot production unit of M/s Ashim Filters, Allahabad to whom our process for the manufacture of rigid sand filters has been released, went into operation. One of our scientists was present for attending to teething troubles in starting the unit.

Large quantity of phenolic resins has been prepared and utilized for the preparation of two sand filter slabs each measuring 24"x24"x3". One of these slabs has been sent to Bombay Municipal Corporation for its use in water filtration at their Powai Water Works.

A few experiments for preparing sand filters using dry powdered phenolic resin have been carried out and preliminary observations are encouraging.

Development work on the resin bonding of small waste-pieces of porous glass slabs (Cell-O-Therm) into bigger sheets has been undertaken on behalf of M/s Techni-Glass Ltd.. Bombay.

3. Polyurethanes (Dr.N.D. Ghatge)

a) Flexible foams (1958)

To develop suitable polyether and polyester resins from indigenous raw materials for making flexible polyurethane foams.

It has been decided to take up this work at a later date.

b) Polyurethane printing rollers (1960)

To develop suitable printing rollers using castor oil.

The process is now given to two parties, one in Poona and the other in Calcutta to undertake the production of the printing rollers.

c) Polyurethane Base Rocket Fuel Binders (1963) (Dr. Ghatge)

To prepare polymeric formulation for the preparation of composite rocket propellants.

A formulation using indigenous materials as far as possible for making composite propellants has been perfected. But in the light of the recent discussion with the Director, E.R.D.L., Kirkee, it has now been decided to modify the above formulation to suit the requirements of ERDL.

d) Coatings (1963) (Dr. Ghatge)

To prepare coatings for specific uses on nylon in collaboration with other organizations/laboratories.

Polyurethane formulation based on polyester-polyisocyanate for coating on nylon has been evaluated by SASMIRA. The rubber produced by the above formulation has good properties. However, the formulation is to be modified to make it much more viscous, suitable for application on the nylon fabric.

e) Adhesives (1965)

To develop suitable isocyanate base adhesive needed for defence, rubber industry and footwear industry.

Polyisocyanates containing phosphorous and triazine ring are to be synthesized. Work is under progress.

D) Surface Coatings (Dr.S.L. Kapur)1. Styrenated alkyds (1963)

Test reports on our alkyd, received from various parties, suggested the desirability of reducing the drying time of our resin and attempts have been made to improve the same. A satisfactory composition of the alkyd resin based on short and medium oil length has been found to meet the requirement in all respects and 9 kg. of this modified styrenated alkyd have been prepared. Films of the resin solution (50% N.V) dry in less than 5 minutes (touch dry) and become tack-free in less than 15 minutes. Samples of the resin (8 kg.) have been supplied to five parties for their trials. One of the parties was supplied with white enamel also prepared from the same resin. Reports of these trials are awaited.

2. Modification of lac (1960)

As reported earlier, the isocyanate intermediate prepared by reacting toluene diisocyanate (TDI) with glycerol and

NCO:OH:2:1). Films from this composition had excellent chemical resistance but poor flexibility. During the period under review, a few compositions have been prepared to improve the flexibility and to find out the chemical resistance of the films from shellac adducts. Thus, TDI has been reacted with different types of polyols of short and long chain such as butane-diol, polyethylene glycol and trimethylol propane. Reaction products of these polyols are then reacted with shellac (in the ratio of NCO:OH:2:1) wherein the hydroxyl groups of lac react with the free NCO groups of the polyol-TDI, reaction products. The films made from these compositions possessed good flexibility but were generally poor in chemical resistance. Butyl ester of shellac having an acid value of less than 10 and containing only hydroxyl groups was reacted with the isocyanate intermediate based on glycerol, TDI and DEG. The films had good flexibility, hardness, good water and alkali (NaOH) resistance but failed in solvents. Further work to improve these films properties is in progress.

3. Linseed oil emulsion (1964)

Preparation of emulsions from linseed oil for coating applications has been attempted. Refined and bleached linseed oil is vacuum-bodied whereby its viscosity increases considerably. Emulsions prepared from this oil become unstable after about 4 weeks of storage. The emulsion has good coating properties, particularly for masonry work. Further work to improve the stability of the emulsion and standardization of the process is in progress.

4. Coating of steel tapes (1964)

After receiving report on the coated steel tapes prepared at the laboratory, one gallon sample of the coating composition has been prepared and supplied to M/s Hindustan Cables, for large scale trials, at their end. Report on its use is awaited.

NCO:OH:2:1). Films from this composition had excellent chemical resistance but poor flexibility. During the period under review, a few compositions have been prepared to improve the flexibility and to find out the chemical resistance of the films from shellac adducts. Thus, TDI has been reacted with different types of polyols of short and long chain such as butane-diol, polyethylene glycol and trimethylol propane. Reaction products of these polyols are then reacted with shellac (in the ratio of NCO:OH:2:1) wherein the hydroxyl groups of lac react with the free NCO groups of the polyol-TDI, reaction products. The films made from these compositions possessed good flexibility but were generally poor in chemical resistance. Butyl ester of shellac having an acid value of less than 10 and containing only hydroxyl groups was reacted with the isocyanate intermediate based on glycerol, TDI and DEG. The films had good flexibility, hardness, good water and alkali (NaOH) resistance but failed in solvents. Further work to improve these films properties is in progress.

3. Linseed oil emulsion (1964)

Preparation of emulsions from linseed oil for coating applications has been attempted. Refined and bleached linseed oil is vacuum-bodied whereby its viscosity increases considerably. Emulsions prepared from this oil become unstable after about 4 weeks of storage. The emulsion has good coating properties, particularly for masonry work. Further work to improve the stability of the emulsion and standardization of the process is in progress.

4. Coating of steel tapes (1964)

After receiving report on the coated steel tapes prepared at the laboratory, one gallon sample of the coating composition has been prepared and supplied to M/s Hindustan Cables, for large scale trials, at their end. Report on its use is awaited.

E) Rubber1. Preparation of modified rubber (1964) (Dr.S.L. Kapur)

As reported earlier, large quantities of modified rubber were prepared and its physical properties (tensile, modulus, ageing) were determined. The results indicate that the incorporation of proteins improves physical properties; tensile strength and modulus increase by about three times over that of pale crape. This procedure could be adopted at the site of collection of rubber latex. Findings of these experiments are being tabulated for publication.

2. Sponge textiles (1964) (Dr. Kapur)

A spreading machine (suitable for this work) has been fabricated by the workshop as per our design. Trial runs have been taken and a few modifications have been found necessary. With the hand operated spreading machine, a few samples of sponge textiles have been prepared. However, the work had to be stopped temporarily due to a major break-down in the planetary mixer (procured indigenously). The spreading machine is now being standardized for continuous operation.

3. Antioxidant for rubber (1963) (Dr.Ghatge)

To develop indigenous antioxidants from CNSL derivatives and their evaluation in rubber.

The condensation product from tetrahydroanacardol and sulphur monochloride has antioxidant properties for natural rubber. Its evaluation by rubber industries has been done. The antioxidant is comparable to any similar antioxidant in its antioxidant properties.

In our studies, it has been found that the condensation product is a mixture of phenol monosulphide and phenol disulphide.

F) CelluloseGrafting on cellulose (1965) (Dr. Kapur)

Studies have been initiated to improve certain properties such as resistance to micro-organisms and mold, and impart anti-crease characteristics to naturally occurring cellulose. This is being attempted by chemical grafting of acrylonitrile and acrylamide on cellulose.

Amongst known methods available for grafting, ceric ion redox system has been selected in view of its leading to minimum degradation accompanied by high percentage of grafting. Cellulose in the form of hanks and paper has been grafted with acrylonitrile and acrylamide using 0.1 N ceric sulfate in 1 N nitric acid at 15-25° for 3-4 hours in an inert atmosphere. The homopolymer is removed by washing with dimethyl formamide at 100° for 15 minutes (in case of polyacrylonitrile) and by washing with hot water (in case of polyacrylamide). The unreacted cellulose is removed by dissolving it in cuprammonium hydroxide solution. The degree of grafting is estimated from increase in weight, nitrogen content and by converting -CN or -CONH₂ groups into -COOH groups by hydrolysis and subsequent estimation of the carboxyl content by back titration with alkali.

The acrylonitrile grafted cellulose samples will be examined for its resistance to micro-organisms. The acrylamide grafted cellulose will be reacted with formaldehyde under suitable conditions whereby crease recovery is expected to improve. The crease recovery characteristics of the grafted cellulose should be better than the conventional practice of mechanical embedding of urea-formaldehyde and melamine-formaldehyde resins in cellulose. Presently, experimental work to standardize the conditions of grafting is in progress.

H) Miscellaneous

1. Large batches of CNSL coating composition for application in table tops prepared and supplied.
2. Samples of cation (CNSL) and anion-exchange (Melamine) resins supplied to CFTRI, Mysore found useful in treatment of grape syrup.
3. Demonstration of process for preparation of chemically resistant covering materials undertaken on behalf of party licensed by NRDC.
4. Preliminary examination of possibility of preparing rubberised cork sheets undertaken on behalf of a private firm.
5. Collaborative work with CIPHERI field unit continued for treatment of H.E. Factory, Kirkee.
6. Preparation of dry foundry core binder, core gum and barrier cream (core cream) have been undertaken. Evaluation of the core cream by industry is to be undertaken.

CHEMICAL ENGINEERING STUDIES

A) Process Development1. Acetanilide (1965) (Dr.L.K. Doraiswamy)

Work has been carried out on a bench scale to develop a process for the production of acetanilide with the ultimate object of collecting enough data for the design of a plant for HOC. When the process conditions are standardized, pilot plant work is carried out on a scale of about 20 kg. per batch. A number of runs have been carried out and a consistent yield of 97% acetanilide (99.6% purity) based on the aniline used has been obtained.

Material balance, energy balance, time schedule, equipment flowsheet, utilities requirement and other relevant data have been passed on to a project engineering firm who have since submitted a tender to HOC for a plant of 2000 tons per year.

A sample of acetanilide from a pilot plant batch (without further purification) has been sent to M/s May & Baker and a satisfactory report has been obtained from them. Another 60 kg. of the material have been sent to the Synthetic Drugs Project (IDPL), Hyderabad, for their use and report.

2. Dibutyl phthalate (1965) (Mr.A.D. Deshpande)

Bench scale investigations have been started on the preparation of dibutyl phthalate by the batch process to gather process data. Initial experiments have been conducted using sodium bisulphate as water-absorbent. Later runs have been carried out using benzene or toluene as an azeotropic agent for the removal of reaction water. Finally, it has been decided to avoid the use of any entrainer but to use excess butanol (under a slight vacuum) for the purpose since butanol and water form a minimum boiling azeotrope. Several runs have been carried out in a 20 litre all-glass distillation unit specially modified for the reaction to study the effect of process variables on product yield and colour. Optimum conditions of temperature, mole ratio and catalyst concentration have been found out. The processing of the crude to almost colourless DBP involves a number of steps all of which are standardized.

3. Diethyl phthalate (1965) (Dr.M. Goswami)

Work on developing a process for the production of diethyl phthalate has been started on a priority basis. Five experiments have been carried out in which benzene and toluene have been used as entrainer for removal of the water of reaction. The reaction takes about 5 hours for completion.

without entrainer, using a higher percentage of sulphuric acid as catalyst and removing the water of reaction under vacuum. The reaction time has been cut down immensely. Processing of the phthalates have been carried out to get a standard colourless product.

Several pilot plant runs have been carried out, each of about 15 kg. per batch of phthalate. The crude products obtained are of better quality than those obtained in the bench scale.

For both the phthalates material, energy balances, time schedules, equipment flowsheets, utilities requirements, peak load figures and other relevant data have been passed on to a firm of project engineers in Bombay.

4. Vitamin B₆ (1960) (Mr.G.V. Potnis)

The detailed report on the pilot plant work carried out so far on the production of vitamin B₆ has been prepared. On the basis of the results obtained in this investigation, approximate cost calculations of the process have been worked out. The requirements of the raw materials and the equipment for a plant to produce annually 2000 kg. of vitamin B₆ have been worked out for M/s Unichem Laboratories Ltd., Bombay, with whom negotiations regarding release of the process are in progress. The preliminary material balance and equipment flow sheets for the process have been prepared.

5. Vitamin C (1957) (Mr.M.V. Kunte)

A process for the synthesis of vitamin C starting from sorbitol was worked out in the Biochemistry Division on the laboratory scale. The object of this project is to work out the process on the pilot plant scale, introduce modifications for its translation to plant scale and collect design data. Work to determine optimum process conditions for the hydrogenation of glucose to sorbitol has also been undertaken.

The process has been worked out on the pilot plant scale and modifications introduced where necessary. Based on this, material balance and process flow-sheets equipment specifications and cost estimates for a 50 t/year plant have been worked out and a complete project report prepared. The process has been

been rendered to them to prepare a project report. They are carrying out larger pilot plant trials and necessary help is being rendered to them. The process for the hydrogenation of glucose to sorbitol has been worked out and tested on the pilot plant scale. A project report on this step has also been prepared.

With a view to reduce the cost of sorbitol, experiments for the direct hydrogenation of starch hydrolysate to sorbitol (without isolation of crystalline glucose) have been continued. However, the fermentability of the sorbitol so prepared is comparatively less. It, therefore, appears that the isolation of crystalline glucose cannot be avoided.

Life test on the Raney catalyst for the hydrogenation of glucose to sorbitol has been carried out under conditions already established. The activity is constant upto eight reuses after which it tends to decline steadily.

The use of higher temperature in oxidation step to minimize the refrigeration load is confirmed by carrying out two pilot scale oxidation runs.

Laboratory scale runs have shown no deleterious effect when crude ascorbic acid obtained in cyclization step has been air dried instead of vacuum drying so far followed. This has been confirmed in two pilot scale runs using chloroform as solvent in one and benzene in the other. Yields in both cases are normal, although the latter product is comparatively darker in colour.

Three large scale recrystallizations (approx. 5kg per batch of crude ascorbic acid) have been carried out, using an all-glass flash evaporator fabricated in the laboratory for concentrating the solutions. Pure ascorbic acid has been recovered in over 90% yield.

One fermentation of sorbitol to sorbose has been

for recovering the sorbose.

Work on the improvement of the various steps in the process and cooperation with HAL in their pilot plant work will be continued.

B) Process Design (Dr.L.K. Doraiswamy)

1. Hexachloroethane

The hexachloroethane process has been sold to a firm in Gujarat. The complete process design of a plant of 500 tons per year capacity has been commenced.

2. Dimethylaniline

Based on the data obtained on a bench scale and a few runs made on a pilot plant scale, the complete process design of a plant of 600 tons per year capacity has been commenced.

3. Acetanilide

Complete chemical engineering designs for a plant of 2000 tons per year capacity have been handed over to a firm of project engineers in Bombay.

4. Phthalates

Chemical engineering designs for a plant of 10000 tons per year capacity for dibutyl and dioctyl phthalates have been made and the calculations are being finalised.

5. Opium alkaloids

The project engineering of the NCL process has been entrusted to the Technological Consultancy Bureau by the Finance Ministry. All the necessary assistance is being given to TCB in their work.

C) Thermodynamics, Kinetics and Reactor Design (Dr.Doraiswamy)

This is a continuing research programme. The objects of this scheme are : development of methods for the prediction of thermodynamic and transport properties; study of the kinetics of different types of reactions; and chemical reactor analysis.

1. Thermodynamics

A new method has been developed for estimating the viscosity (an important transport property) of any substance over a wide range of temperature and pressure. In this development the importance of the critical compressibility as a correlating parameter has been recognised and appropriate charts prepared for different values of the critical compressibility.

A completely general method has been developed for estimating the density of liquids from critical properties using the expansion factor of Watson. The expansion factor has itself been found to be a function of the critical compressibility and allowance has been made in the correlation for changes in the critical compressibility.

A new theoretical equation has been developed for estimating the diffusivity of a substance in a liquid starting from Eyring's diffusion equation. This equation predicts the liquid diffusivity to within about 18%.

Further work in this area is aimed at developing procedures for heat of fusion, entropy formation, thermal conductivity and other important thermodynamic and transport properties.

2. Kinetics

Work is in progress on the determination of the mechanism of the hydrogenation of anacardol (obtained from cashewnut shell liquid) to tetrahydroanacardol in a vibratory reactor. The experimental assembly has been set up and runs have been carried out on the effect of mass transfer.

Work on the mechanism of the dehydration of ethanol over Indian bauxite has been completed. The investigation has now been extended to the dehydration of hexanol, after which the dehydration of butanol, pentanol and other aliphatic alcohols up to C₁₀ will be studied with the object of establishing the effect

of

The kinetics of the hydrogenation of o-nitrotoluene to o-toluidine has been investigated and a probable reaction model has been established. It is proposed to extend this work to the hydrogenation of p-nitrotoluene to p-toluidine using the same catalyst.

Work on the oxidation of aromatic hydrocarbons (benzene and toluene) is in progress. A new mechanism for oxidation which incorporates both the Hinshelwood steady-state theory and the Heugen-Watson limiting-step theory is being developed. The mechanism of oxidation is being examined for different catalyst compositions in order to study the change of mechanism with the proportion of catalyst ingredients.

A new MT reactor has been set up and the oxidation of benzene is being studied in this reactor system. It is believed that this reactor will be optimum for reactions of this type. Experimental verification of the optimality criterion is being sought.

3. Reactor design and fluidization

An experimental assembly is being fabricated to investigate the use of fluidization as a means of heat transfer in large reactors. The introduction of small-diameter reaction tubes (which will act as vertical surfaces) is expected to improve the quality of fluidization. If this method of heating is found to be successful, then the design and operation of multi-tubular reactors will be greatly facilitated, particularly when a uniform heat flux is desired.

Work on the theoretical and experimental aspects of semi-fluidization is in progress. A technique has been developed with the assistance of the Instrumentation Section to measure the quality of fluidization as the region of semi-fluidization is approached and the mixed reactor system becomes operative.

D) Mass Transfer

The extensive data available on liquid-liquid extraction is being statistically analysed to determine a suitable equation for predicting the onset of flooding. Work on the effect of pulsation and hold up on flooding has been completed and the general flooding equation will be modified to incorporate the effect of pulsation.

A complete literature survey has been made on the use of fluidization in extraction and absorption apparatus. A suitable apparatus for fluidized absorption has been designed and is being erected.

It is believed that a substantial portion of mass transfer occurs during drop formation in liquid-liquid extraction. Exhaustive data have been collected using the system benzene-water-acetic acid and the proportion of mass transfer occurring during drop formation is being determined. Attempts are being made to incorporate new techniques for the measurement of mass transfer during drop formation and collapse. The data will be correlated using a modified unsteady-state diffusion equation.

5. OPERATIONAL RESEARCH, INDUSTRIAL
LIAISON AND EXTENSION

A. Research Schemes Sponsored by Industry or Outside Agencies.a) Schemes continued from April 64 to March 65:

Manufacture of calcium hypophosphite	M/s Chunilal Ootamchand & Co., Bombay.
Constitution of lac	Lac Research Institute, Ranchi.
Manufacture of acriflavine	M/s Bhaidas Karsandas & Co., Bombay.
Research on commercial uses of Punjab costus (Kuth) root	Government of Punjab
Manufacture of golden yellow G.K.	M/s Amar Dye Chem. Ltd., Bombay.
Chemical and thermodynamic properties of refractory materials under PL-480	National Bureau of Standards, Washington.
Investigation of the effect of heat on tung oil and derivatives of tung oil and the characterisation and identification of compounds resulting from heat treatments to extend the utilisation of tung oil under PL-480	U.S. Department of Agriculture.
Work on investigations of the synthesis and properties of new type glycol monoalkyl ethers for the control of water evaporation, to extend the industrial utilisation of cotton seed oil under PL-480.	U.S. Department of Agriculture.
Reactive dyes	M/s Amar Dye Chem. Ltd., Bombay.
Lac dye	Lac Research Institute, Ranchi.
Composite drug research scheme on Indian medicinal plants	Ministry of Health, Govt. of India, New Delhi.
Manufacture of diethyl-m-aminophenol	M/s Sahyadri Dyestuff & Chemicals (P) Ltd., Poona-2.

b) Schemes completed during April 65 to Sept. 65:

Isolation of Berberine (hydrochloride) from berberis bark.	M/s G. Vallabhadas & Co., Bombay.
--	-----------------------------------

c) Schemes undertaken during April-September 65:

Improvements in the process for the manufacture of l-menthol from de-mentholised peppermint oil. M/s Bhavana Chemicals Ltd., Baroda.

Titanium tetrachloride from ilmenite M/s Travancore Titanium Products, Triyandrum (Kerala).

Studies in pine oil from Indian turpentine oil M/s Prabhat General Agency, Bombay.

Fabrication of electron diffraction camera Three different parties.

B. Projects Completed during April-September 65:

Acetanilide

Diocetyl phthalate

Dibutyl phthalate

C. Patents and Processes Passed on to Industry:

nil

D. Project Reports, Design Data etc. Supplied:

Desiccant type silica gel M/s Minco Products, Madras.

This process was completed in 1962 on behalf of the firm. Detailed process write-up and flow-sheet diagrams have been supplied.

Vitamin B₆ M/s Unichem Laboratories Ltd., Bombay.

List of equipments and raw materials for a plant to produce 2 tons/year has been supplied.

E. Technical Enquiries Answered:

Government organisations ... 106

Private firms & individuals... 110

Total 216
=====

F. Work done for outside Parties (Universities/Research Institutes/Govt. Departments, Private Parties etc.)a) Supply of cultures

355 cultures from NCIM were supplied to various parties on their requests.

b) Analytical/testing services:

Following types of analytical and testing services were rendered to several parties during April-September 65:

Microanalysis 67 samples

Vapour phase chromatographic analysis 5 "

Infra-red spectral analysis 27 "

Ultra-violet spectral analysis 10 "

X-ray diffraction patterns 4 "

Nuclear magnetic resonance 24 "

c) Technical aid involving adhoc, experimental work, instrumental, engineering and glass blowing services:

6 mercury pulse delay tanks for IAF radars, Poona-6 were reconditioned (at Rs.700/- each).

A Brookfield viscometer repaired for Defence Research & Development Organisation, Poona. (Charges Rs.75/-)

A photometer repaired for Maharashtra Engineering Research Institute, Nasik. (Charges Rs.50/-)

A sample of tungsten carbide analysed for impurities for M/s Sandvic Asia Ltd., Chinchwad.

A sample of adhesive for backlite to rubber based polyurethane supplied to M/s Gannon Electronics, Bombay for evaluation.

A sample of adhesive for PVC to rayon was supplied to M/s Pendse & Co., Poona for evaluation.

Coating composition for steel strips was prepared and sent to M/s Hindustan Cables, Bardwan, for trials.

Nylon powder was prepared (from nylon waste) and sent to M/s Manohar & Co., Hyderabad, for trials.

Large scale experiments on prevention of the sediment formation in storage of grape juice and preparation of wines from the same was completed for CFTRI, Mysore.

Three patients from AFMC, Poona were examined for possible thyroid disorder by measuring the uptake of radioactive iodine; and, percentage absorption of radioactive cobalt labelled vitamin B₁₂ was measured in two anaemic patients.

A sample of ion exchange resin was sent to CFTRI, Mysore for investigation.

150 g. of epoxy resins were supplied to M/s Angelo Bros., Calcutta, for trials.

In collaboration with CIPHERI, Nagpur, work has been continued on "H.E. Factory acid waste" with the treatment of ion

Sample of polyurethane base coating for nylon was supplied to SASMIRA, Bombay for evaluation.

More samples of modified indigenous gum were sent to Post & Telegraph Board, New Delhi, for actual trials.

G. Industrial Surveys and Collection of Statistical, Economic and Market Data etc.

Cost data on centrifugal pumps was collected and simplified technique for estimating its costs has been found out.

H. Extension Work:

Following non-technical notes on processes developed in NCL have been supplied to various parties:

Sugarcane wax; theophylline; vitamin B₆; polyurethane printing rollers; nicotine sulphate; ethyl acetoacetate; BON acid; barium and strontium chloride; foundry core oil; thermistors; sorbitol; sisal wax; rubber base adhesive; liquid rubber; soft ferrites.

One kg. of clear sand and resin bonded sample of porous rigid filter was sent to M/s Hyderabad Laminated Products, Secunderabad, for evaluation.

A sample of rocket fuel binder was sent to Birla Institute of Technology, Ranchi, for evaluation.

A sample of polystyrene cation exchange resin sent to Indian Institute of Science, Bangalore, for evaluation.

Sample of berberine acid sulphate was prepared and supplied to M/s Bombay Alkaloids Pvt.Ltd, Bombay.

Modified styrenated alkyd solution prepared and sent to six paint manufacturers and also to Research, Designs & Standards Organisation, Chittaranjan, to test its suitability in paint formulation.

A sample of sorbitol solution (70%) was sent to M/s Kanak Chemical Industries, Calcutta, for trials.

I) Visits of NCL Scientists to Industry for Project Follow-up or for General Visit:

Scientists	Industry visited	Subject
Mr.S.N. Balasubramanian Mr.S.P. Mukherjee	Six industries in and around Calcutta	General visit
Dr.S.K. Subramanian	Seven industrial units in Madras, Vijayawada & Bangalore.	Project follow-up work.
Dr.S.K. Subramanian Mr.N.K. Buzruk	M/s Chemaux Pvt.Ltd., Bombay.	Bacterial diastase.
Dr.B.D. Tilak	M/s A. Lajjee, Bombay.	Sulphur blue dyes project.
Dr.B.D. Tilak	M/s Hico Products, Ltd., Bombay.	X X X
	M/s Aniline Dyestuffs & Pharmaceuticals, Bombay.	X Discussions X X X
	I.C.M.A., Bombay.	X
Dr.S.K. Subramanian	M/s Aphali Pharm. Ltd., Ahmednagar.	Sisal wax
Mr.M.V. Kunte Mr.H.G. Vadgaonkar Mr.S. Chidambaran	Hindustan Antibiotics Ltd., Pimpri	Assistance in large scale pilot plant of vit. C
Mr.N.K. Buzruk Mr.G.V. Potnis	M/s Indian Organic Chemicals Ltd., Khopoli.	Semi-commercial plant of ethyl acetoacetate.
Mr.V.V. Indushekhar	M/s Ashim Filters, Allahabad.	Production of rigid filters.
Dr.L.K. Doraiswamy Dr.B.D. Tilak	Indian Dyestuffs Industry Ltd., Bombay.	X X In connection X with some HOC X work.
	M/s Amar Dye Chem. Bombay.	X X
Dr.P.K. Bhattacharyya Dr.S.K. Subramanian Dr.B.D. Tilak	M/s Indian Scherring Ltd, Bombay.	Some proposed sponsored work.
Mr.D. Chakrabartty Mr.S.S. Mahajan	C.G.C.R.I., Calcutta.	To find out the possibility of the supply of refractory materials manufactured by them and to study the high temperature furnaces in operation there.
Dr.J. Gupta Dr.V.V. Dadape Dr.V. Damodaran Mr. I. Kumville	A.E.E. Trombay, Bombay.	To chalk out coordinated programme for the beneficiation of Indian ilmenite.

Mr. Lakhbir Singh	R.R.L. Hyderabad	X X X X	Discussions and general visit.
Mr. A.M. Chavan	M/s Western India		
	Vegetable Products,		
	Amalner.		

J) Demonstrations:

Following demonstrations on NCL processes have been given:

M/s Natson Manufacturing Co., Ahmedabad.	Acid resistant covering materials from CNSL.
M/s Saraswati Press, Calcutta.	Polyurethane printing rollers.
M/s Indian Organic Chemicals, Khopoli.	Ethyl acetoacetate.

K) Training/Guest Workers:

<u>Party</u>	<u>Trained in</u>
Students from IIT, Bombay.	Glass blowing technique.
Students from SIRI, Poona.	- do -
Dr. V.P. Gupta, Lucknow University.	Techniques of operating light scattering photometer.
Mr. A.S. Chauhan, Roorkee University.	- do -
Mr. P.V. Somayajulu, Engineering College, Warangal.	Microanalysis and spectroscopy.
Mr. R.L. Handa, IART, New Delhi.	Chromatography techniques.
Mr. O.N. Devgan, Vikram Univer- sity, Ujjain.	- do -
Mr. Deol, Agriculture Univer- sity, Ludhiana.	VPC techniques.
Mr. D.C. Jain, Ministry of Industry and Supply, Ambala.	Glass blowing techniques.

Following guest workers from various universities, insti-
tutes, worked in NCL for varying periods:

Mr. A.S. Chauhan, Roorkee University.
Mr. J.P. Shukla, Jabalpur University.
Mr. R.L. Handa, IART, New Delhi.
Mr. P.V. Somayajulu, Engineering College, Warangal.
Mr. O.N. Devgan, Vikram University, Ujjain.
Mr. Deol, Agriculture University, Ludhiana.

L) Special Fabrications:

One thin film evaporating unit (approx. price Rs.15,000/-).

Warburg flask (approx. price Rs.500/-).

Glass reactor for diemethylaniline plant
(approx. price Rs.1000/-).

A dual column vapour phase chromatograph with a thermal
conductivity detector and facility for temperature
programming was developed and a prototype model fabricated.
Comparative tests made with other gas chromatographs
available in the NCL show that our chromatograph is
comparable in performance to the imported instrument.

An electron spin resonance spectrometer working in the
X-band microwave region was completed. Measurements
indicate that it is capable of detecting 10^{13} spins/ ΔH
which is sufficient for carrying out a majority of the
measurements in ESR.

Eleven exhaust blowers (gallen Kemp type)
(approx. price Rs.950/- each).

One stainless steel paint grinding pot (approx.
price Rs.200/-).

One vertical gas cylinder trolley for one cylinder
(approx. price Rs.100/-).

One stainless steel ball mill (approx. price Rs.350/-).

One opium exhausting unit consisting of 3 jacketed
stainless steel vessels with driving arrangement mounted
on M.S. stand (approx. price Rs.2000/-).

One stainless steel bleacher mounted on M.S. stand with
driving arrangement (approx. price Rs.2800/-).

One M.S. trolley for vacuum pump (approx. price Rs.300/-).

Three thin layer applicators with base plates
(approx. price Rs.360/- each).

6. PUBLICATIONS AND PATENTS:

A. Publications:

1. Jose (Mrs.), Parimala and Pant, L.M. The crystal and molecular structure of β -alanine. Acta Crystallographica, 18, part 4, 806 (1965).
2. Joshi, A.W. and Sinha, K.P. Phonon-magnon relaxation processes in ferrimagnetic systems. Proceedings of physical Society (London). Supplement for the 1964 magnetism conference, 411 (1965).
3. Deo, A.V., Kulkarni (Miss), S.B., Gharpurey, M.K. and Biswas, A.B. Specific resistance of the monolayers of n-long chain alcohols and n-long chain alkoxy ethanols to the evaporation of substrate water molecules. Ind. J. Chem. 5, 200 (1965).
4. Narasimhan, K.S.V.L. and Sinha, K.P. Spin effects in bismuth telluride doped with magnetic impurities. Ind. J. Pure Appln. Phys. 3, 6, 221 (1965).
5. Pryce, M.H.L., Sinha, K.P. and Tanabe, Y. On the tetragonal distortion of octahedral systems in an E_g electronics state. Molecular Physics 9, 1, 33 (1965).
6. Sharma, V.S., Mathur, H.B. and Kulkarni, P.S. Stability of transition metal complexes of amino acids. Ind. J. Chem. 3, 4, 146 (1965).
7. Badachhape, R.B., Gharpurey, M.K. and Biswas, A.B. Density and surface tension of phenol (mono-, di- and tri-) chlorophenols, salol and (o- and m-) chloronitrobenzenes. J. Chem. Eng. Data 10, 2, 143 (1965).
8. Gopal Rao, R.V. Phenomenological theory of surface tension and compressibility: Evaluation of the parameter. Ind. J. Pure & Applied Physics 3, 7, 233 (1965).
9. Goswami, A. Oxidation of metals in air and reduced pressures. Ind. J. Chem. 3, 8, 385 (1965).
10. Sakore, T.D. and Pant, L.M. Preliminary structure analysis of p-nitrobenzoic acid. Ind. J. Pure Applied Physics 4, 143 (1965).
11. Sen, D.N. and Thankrajan, N. Aluminium nitrate and nitric acid as nitrating agents for acetylacetonates. Ind. J. Chem. 3, 5, 215 (1965).
12. Gopinathan, C. and Gupta, J. Organoxy-titanium compounds. Ind. J. Chem. 3, 5, 231 (1965).
13. Chandra (Mrs.), Sarswati and Roy Chowdhury, P. Ultrasonic degradation of butyl rubber in solution. Ind. J. Chem. 3, 3, 338 (1965).
14. Homawala (Miss), T.K., Shetty, P.S. and Subbaraman, P.R. Idometric estimation of gold. Ind. J. Chem. 3, 8, 248 (1965).
15. Joseph Kuruvilla and Dadape, V.V. Studies in the chlorination of Indian bauxite ores. Ind. Technol. 3, 8, 244 (1965).
16. Joshi, B.S., Ramanathan, S. and Venkataraman, K. Endocrocin. Bulletin of the National Institute of Sciences of India. No.28, 122 (1965).
17. Bhide, N.S., Joshi, B.S., Patwardhan, A.V., Srinivasan, R. and Venkataraman, K. Lac pigments. Bulletin of the National Institute of Sciences of India No.28, 114 (1965).
18. Kapadia, V.H., Nagasampagi, B.A., Naik, V.G. and Sukh Dev. Studies in sesquiterpenes - XXVI - Structure of muskatone and copaene. Tetrahedron 21, 6057 (1965).
19. Kapadi, A.H. and Sukh Dev. Chemical transformation of (+)-hibaene into (-)-kaurene. Tetrahedron Letters No.18, 1225 (1965).
20. Radhakrishnan, P.V., Rama Rao, A.V. and Venkataraman, K. Two hawones from Artocarpus heterophyllus. Tetrahedron Letters No.11, 663 (1965).
21. Janaki (Miss), N., Pathak, K.D. and Subba Rao, B.C. Reductions with diborane and sodium borohydride-lewis acid complexes - part III - Hydrogenolysis of acetals and ketals. Ind. J. Chem. 3, 3, 123 (1965).
22. Modi, B.D. and Bose, J.L. Simple spot tests for vanillin and some other carbonyl and chelated hydroxy compounds. Ind. J. Chem. 3, 5, 236 (1965).
23. Sonawane, H.R., Naik, V.G., Subba Rao, B.C. Boronfluoride catalysed alkylations of phenol - part I - Alkylation with isomeric octanols, octenes and octyl bromides. Ind. J. Chem. 3, 6, 260 (1965).
24. Kapadi, A.H., Sobti, R.R. and Sukh Dev. The diterpenoids of erythroxyton monogynum V, atisirene isoatisirene and devadarene. Tetrahedron Letters No.31, 2729 (1965).
25. Kaul, B.L., Srinivasan, R. and Venkataraman, K. Structures of azoic coupling compounds and azoic dyes. Separatum of Chemia 19, 213 (1965).
26. Damodaran, N.P. and Sukh Dev. Stereochemistry of zerumbone. Tetrahedron Letters 24, 1977 (1965).
27. Narayanan, C.R. and Iyer, K.N. Mode of cleavage of steroid methyl ether with BF_3 -Etherate. Tetrahedron Letters No.19, 1369 (1965).
28. Subba Rao, V.V. Calcination and sintering study of ceria. Ind. J. Chem. 3, 8, 343 (1965).
29. Chetty, G.L. and Sukh Dev. Mayurone, a C_{14} sesquiterpene ketone. Tetrahedron Letters No.42, 3773 (1965).
30. Narayanan, C.R. and Iyer, K.N. Regeneration of steroid alcohols from their methyl ethers. J. Org. Chem. 30, 1735 (1965).

31. Narayanan, S.S., Welankiwar, S.S., Kulkarni, S.N. and Bhattacharyya, S.C. Synthesis of CIS norbergamotinic acid. Tetrahedron Letters No.15, 985 (1965).
32. Ranibai (Miss), P., Kamat, S.Y., Ghatge, B.B., Chakravarti, K.K. and Bhattacharyya, S.C. Terpenoids LXV. Transformation in the santalene longifolene series. Tetrahedron 21, 3, 629 (1965).
33. Mehra, M.M., Ghatge, B.B. and Bhattacharyya, S.C. Terpenoids LXVI. Ring enlargement produced by the alkaline fusion of W-bromolongibolene. Tetrahedron 21, 3, 637 (1965).
34. Kulkarni, K.S. and Rao, A.S. Terpenoids LXVII. Synthesis of a ketodicarboxylic acid related to elemol and epidihydroendesmol. Tetrahedron Letters No.2, 1167 (1965).
35. Bapat, B.V., Ghatge, B.B. and Bhattacharyya, S.C. Terpenoids LXIV. Evaluation of polyesters as stationary phases in gas-liquid chromatography of terpenoids. J. Chromatography 18, 308 (1965).
36. Chakravarti, K.K. Stereochemistry of khusilal. Ind. J. Chem. 3, 7, 324 (1965).
37. Chakravarti, K.K. Stereochemistry of the derivatives of khusinol. Ind. J. Chem. 3, 7, 325 (1965).
38. Chakravarti, K.K., Nayak, U.G. and Bhattacharyya, S.C. Macrocyclic musk compounds - part VII - New synthesis of civetone dicarboxylic acid and its conversion to trans-civetone. J. Chem. Soc. 2475 (1965).
39. Mathur, H.H. and Bhattacharyya, S.C. Macrocyclic musk compound. part IX - New synthesis of cyclohexadecenone. Tetrahedron 21, 1537 (1965).
40. Bawdekar, A.S. and Kelkar, G.R. Terpenoids LXVIII. Structure and absolute configuration of costic acid, a new sesquiterpenic acid from costus root oil. Tetrahedron 21, 1167 (1965).
41. Honwad, V.K. and Rao, A.S. Terpenoids LXIX. Absolute configuration of (-) α -curcumene. Tetrahedron 21, 1167 (1965).
42. Honwad, V.K. and Rao, A.S. Terpenoids LXXII. Synthesis of (\pm) α -curcumene and related compounds. Current Science 18, 534 (1965).
43. Rao, A.S. Terpenoids LXXIV. A synthesis of (\pm) curcumene. Ind. J. Chem. 3, 419 (1965).
44. Sadana, J.C. and Rittenberg, D. Iron requirement for the hydrogenase of desulfovibrio desulfuricans. Archives of Biochem. Biophys. 108, 255 (1964).
45. Dhawalikar, R.S. and Bhattacharyya, P.K. Microbiological transformations of terpenes V. The origin of 2-nonene-2,3-dicarboxylic acid anhydride. Ind. J. Biochemistry 2, 6, 73 (1965).
46. Altekar (Mrs.), W.W., Bhattacharyya, P.K., Maskati (Miss), F.S. and Rao, M.R.R. Aconitate isomerase in sugarcane

47. Ghatge, N.D., and Gokhale, R.G. Development of rubber chemicals on small scale in India. Rubber News, IV, 7, 28 (1965).
48. Krishnaswamy, N. Ion exchange membranes. Synthesis and applications. J. sci. industr. Res. 24, 5, 244 (1965).
49. Dasare, B.D. and Krishnaswamy, N. Studies on anion exchange resins - part II - Preparation and properties of an anion exchange based on cashewnut shell liquid and tetraethylene pentamine. Ind. J. Technol. 3, 7, 212 (1965).
50. Narsimhan, G. A generalized expression for predicting latent heat of vaporization of liquids. Brit. Chem. Eng. 10, 4, (1965).
51. Deshpande, A.D., Thangappan Nadar, R. and Pai, M.U. Fluidization of mixed materials. Ind. J. Technol. 3, 4, 111 (1965).
52. Madhusudana Rao, K. and Pai, M.U. Ternary liquid equilibria of butyric acid-water-ethyl acetate/butyl acetate systems. Ind. J. Technol. 3, 6, 178 (1965).
53. Narsimhan, G. A generalized chart for saturated liquid densities. Ind. J. Technol. 3, 7, 230 (1965).
54. Phadtare, P.G. and Doraiswamy, L.K. Mass transfer model for kolbeschmitt carbonation of 2-naththol. J. I. & EC Process Design and Development 4, 7, 274 (1965).
55. Babu Rao, K., Mukherjee, S.P. and Doraiswamy, L.K. A new adiabatic MT reactor system. A. I. Ch. E. J. 11, 4, 741 (1965).
56. Krishnaiah, M.M., Pai, M.U. and Sastri, S.R.S. Enthalpy concentration diagram for the system carbon tetrachloride chloroform. J. Chem. Eng. Data 10, 2, 117 (1965).
57. Krishnadas, M.S. and Pai, M.U. Equilibria in the oxalic acid - tartaric acid - water system. J. Chem. Eng. Data 10, 2, 97 (1965).

B) Papers sent to Symposia and General Science Papers:

1. Goswami, A. and Koli, S.S. Semiconducting properties of PbTe films. International Symposium on Basic Problems in Thin Film Physics, West Germany.
2. Devkar, V.D. and Goswami, A. Some studies on Hall effects on thin films. International Symposium on Basic Problems in Thin Film Physics, West Germany.
3. Badachhape, S.B. and Goswami, A. Epitaxial growth of cuprous halides on single crystal substrates. International Symposium on Basic Problems in Thin Film Physics, West Germany.
4. Goswami, A. Epitaxial growth and crystal structure. International Conference on Electron Diffraction and Nature of Defects in Crystals, Australia.
5. Nair, P.M., Gopakumar, G. and Fairwell, T. Long range spin-spin coupling in the solid state.

6. Seth, N.D. and Subramanian, S.K. Weeds: A burden on our crops. Chemical Age of India, 16, 764 (1965).
7. Lele, A.M. and Subramanian, S.K. NCL's contribution to industry. Economic Times, 30th June, 1965.

C) Book Review:

1. Review of the Book entitled "Methods in microanalysis" Vol.1, Simultaneous rapid combustion (by J.A. Kuck; Gordon & Braach Science Publishers, N.Y.) by Shri V.S. Pansare (1965).
2. Review of the book entitled "The Mechanics of Aerosols" (by N.A. Fuchs translated from the Russian by R.E. Daisley and M. Fuchs, edited by C.N. Davies Oxford, 1964) by A.B. Biswas (1965).
3. Review of the book entitled "Emulsions: Theory and Practice" (Edition 1965, A.C.S. Monograph No.162, Paul Becher) by A.B. Biswas (1965).

D) Brochures, Booklets etc.

Fine Chemicals Project Catalogue has been published (p.25).

E) Patentsa) Applied

Ghatge, N.D. and Kapur, S.L. † Preparation of poly-urethane printing rollers. Applied in USA - no.434673 corresponding to Ind.Pat. 86991.

b) Filed

Kapur, S.L. and Ramkrishnan, K. An improved method for hydration of sulphonation mixture of copolymer beads. Ind. Pat. 98155.

Kapur, S.L. and Joshi, R.M. Preparation of solvent modified copolymers by suspension polymerization of vinyl monomers. Ind.Pat. 98156.

Paranjape, S.V., Patil, S.G., Potnis, G.V. and Vartak, H.G. An improved process for the recovery of potash from cane molasses before/after fermentation. Ind.Pat. 98153.

Varma, J.P. Process for the manufacture of novel binding agents for core sand. Ind.Pat. 99590.

Ambardekar, D.S. and Biswas, A.B. Process for the preparation of Day-light and Pink-light emitting Electroluminescent Phosphors. Ind. Pat. 101161.

c) Accepted

Momin, Au U. and Sinha, A.P.B. A polycrystalline p-n junction photovoltaic solar cell. Ind. Pat. 89004.

d) Renewed

Sen, D.N. and Gupta, J. A new process for the purification of selenium. Ind. Pat. 56725. Renewed for one year.

Iq'bal, S.F., Lobo, J. and Gupta, J. A direct process for preparing chlorides of barium and strontium from the sulphate minerals. Ind. Pat. 72425, Renewed upto 30.6.66.

Shah, V.R., Bose, J.L. and Shah, R.C. A new process for the production of 4-hydroxycarboystyrls. Ind. Pat. 65777. Renewed upto September 1966.

Joshi, C.G., Bose, J.L. and Shah, R.C. Improvements in or relating in the production of trans-diethylstilbestrol and allied stilbenes. Ind. Pat. 65778. Renewed upto September 1966.

e) Lansed

Shah, V.R., Bose, J.L. and Shah, R.C. New process for the production of 4-hydroxycoumarin and its derivatives. Swiss Pat. 383993. (corresponding Ind. Pat. 62890.)

7. LIBRARY HOLDINGS AND NEW ADDITIONS :

Holding as on 1st Apl. 1965. 45,745

New additions from 1.4.65 to 30.9.65

Books 362

Bound volumes (journals) 2

Thesis 25

Microfilms 3

Patents 17

Translations 8

Photo copies 3

420

420

Grand total 46,165

8. SEMINARS, SYMPOSIA AND EXHIBITION

Every week seminars are held at NCL in which the members of the scientific staff take an active interest. Talks by NCL staff as well as outside eminent scientists are arranged.

a) Seminar lectures given by NCL staff members

Dr. (Miss) M.V. Natekar	17.4.65	Alcoholysis of oils & fats.
Dr. S.K. Dhar	24.4.65	Chemistry of six coordinate silicon compounds.
Dr. C.V. Vishwanathan	1.5.65	Thin layer chromatography.
Dr. P.C. Parthasarathi	22.5.65	Structure and stereochemistry of denudelphenine.
Mr. N. Kumar	19.6.65	Lasers.
Mr. R.K. Gupta	17.7.65	Synthesis of degradation product of Patchouli alcohol.
Dr. V.B. Tare	24.7.65	Uses of zirconium dioxide as a solid electrolyte.
Dr. M.C. Srinivasan	31.7.65	The impact of genetic variation on recent trend in microbiology.
Mr. S. Gundiah	7.8.65	Solution behaviour of randomly branched polyvinyl acetate.
Dr. A.P.B. Sinha	28.8.65	An introduction of high speed digital computers.
Dr. S.C. Bhattacharyya	28-8-65	Impressions of recent visit to USSR.
Dr. K.G. Das	18.9.65	Molecular rearrangements under electron impact.

b) Seminar lectures given by outside eminent scientists

Prof. O.M. Poltorak, Visiting Professor, USSR.	3-6-65	Kinetics of heterogeneous catalytic reactions.
--	--------	--

-do-

	4-6-65	Heat disorder in real crystals and
--	--------	------------------------------------

Prof. O.M. Poltorak, Visiting Professor, USSR.	5-6-65	Electronic theories of catalysis on semiconductors.
Dr. H.R.C. Pratt, CSIRO, Australia.	23-7-65	Process development and chemical engineering research in CSIRO, Australia.
Dr. H.M. McNair, Wilkins Instrument Research Inc., U.S.A.	18.6.65	Preparative scales gas chromatography.
Prof. R.C. Brasted, University of Minnesota, USA.	5-7-65	Optical rotary dispersion of complex compound.
Prof. R.D. DeMoss, University of Minnesota, USA.	7-7-65	Metabolism of tryptophane
Dr. P.A. Ongley, College of advance Technology, Birmingham, U.K.	22-9-65	Chemistry of benzcyclobutene.

c) Lectures given by NCL staff members in universities and other organisations:

Dr. K.P. Sinha (May 65)	Summer School, Nainital.	Spin wave phonon relaxation processes in magnetically ordered system.
Dr. P.R. Subbaraman (May 65)	Summer School Chandigarh.	Polarography of metal-polyphosphate complex
Dr. D.N. Sen (May 65)	Symposium on Inorganic Chemistry held at Chandigarh.	Recent trends in coordination chemistry, quasi-aromaticity, isomerism and specificity of metal chelates.
Dr. A. Goswami (April 65)	Defence Science Lab: Delhi	Physics of thin films.
Dr. A. Goswami (June 65)	Summer Instt. College for Teachers, Bombay.	Electron diffraction.
Dr. N. Krishnaswamy (June 65)	Instt. of Marine Engrs. Bombay.	Saline water conversion by ion exchange technique.
Dr. L.K. Doraiswamy (June 65)	RRL, Hyderabad	Chemical reactor kinetics.

International Symposia held in NCL :

A symposium on 'Recent Advances in the Chemistry of Terpenoids' organized by the National Institute of Science of India and Kurukshetra University was held from June 7th to June 10th. Besides 10 foreign scientists, about 140 scientists from various universities and institutes in India attended the symposia. More than 70 papers were read, out of which 32 papers were contributed from NCL staff members.

9. Visitors

Large parties and many other small groups comprising of 511 visitors were taken round the laboratory and given brief introduction to the nature of NCL work.

Distinguished visitors

In addition to the scientists listed under item 8(b), the following distinguished visitors visited NCL :

Dr. P. V. Cherian, Governor of Maharashtra, Aug. 1965.

10. ADMINISTRATION :

The meeting of the Executive Council of the NCL was held in NCL on 21st and 22nd August 1965 with Prof. T.R. Govindachari in the Chair.

The Council confirmed the minutes of the meeting held on 30th and 31st January 1965.

The Annual Report for the year 1964-65 was approved by the Council with certain observations.

The Council accorded its approval for under-taking the following sponsored research schemes :

1. Pine oil from Indian turpentine oil - by M/s Prabhat General Agency, Bombay.
2. Pilot plant scheme for the production of titanium tetrachloride from ilmenite - by M/s Travancore Titanium Products Ltd., Trivandrum.

The Council accorded its approval for the creation of the following posts with effect from 1st March 1966.

<u>Name of the post</u>	<u>No. of posts</u>	<u>Scale of pay</u>
Joint Director	2	Rs. 2250/-.

The Council also accorded its approval for the creation of one post of Motor Driver in the scale of Rs. 110-3-131-4-139 with immediate effect.

The Council approved the proposal to upgrade the post of Assistant Surgeon Grade I in the scale of Rs. 325-25-500-590-EB-30-800 to the post of Medical Officer in the scale of Rs. 450-30-660-EB-40-1100-50-1250 plus the nonpractising allowance attached to the post.

The Council accorded administrative approval and technical sanction to the construction of a high pressure laboratory at a cost of Rs. 77,332/-.

The Council accorded its approval for the distribution of share of royalties and premia to the investigators and other concerned in respect of all pending cases in accordance with the existing practice.

The Council accorded administrative approval and expenditure sanction in connection with the purchase of apparatus and equipment as under :

Administrative approval

Automatic Amino-acid Analyzer	Rs. 1,00,000
Light Scattering Photometer	Rs. 75,000

Administrative approval and expenditure sanction

Cryodyne helium liquefier	Rs. 1,50,000
High magnetic field equipment	Rs. 1,00,000

The Council approved the action taken regarding the purchase of a Mass Spectrometer and an I.C.T. Computer for the NCL.

Budget

The Council endorsed the following recommendations

of the Building & Finance Sub-Committee and approved

Figures in thousand of rupees

Revised estimates Budget estimates
for 1965-66 for 1966-67

Recurring

PP-1	Pay of officers	1048.0	1300.0
P-2	Pay of establishment	1300.0	1395.5
P-3	Allowances	870.0	950.0
P-4	Contingencies	449.1	400.0
P-6	Maintenance	32.0	35.0
P-7	Chemicals, apparatus & equipment for research.	1200.0	1150.0
A	Total Recurring	4899.1	5230.5

Capital

P-5 (1)	Works	200.0	265.0
P-5 (2)	Services	190.0	265.0
P-5 (3)	Apparatus & equipment	1615.0	850.0
P-5 (4)	Miscellaneous	70.0	100.0
B	Total capital	2075.0	1480.0
C	<u>Pilot Plant</u>	678.0	800.0
	Total A, B and C	7652.1	7510.5

The following meetings of the advisory Panels were held and the proceedings were placed before the Executive Council.

Advisory Panel for Dyes and Dye Intermediate	18-8-65
Advisory Panel for Polymers	19-8-65
Advisory Panel for Chemical Engineering, Process Development and U.N. Special Fund Project	19-8-65
Advisory Panel for Rayon Grade Pulp Project	19-8-65

It was decided that the Rayon Grade Pulp Project should be renamed as " Dissolving Pulp Project ".

The Council constituted a Panel for Radiation and Nuclear Chemistry comprising (1) Prof. H.J. Arnikar (2) Dr. Jagdish Shankar (3) Dr. Brahm Prakash (4) Dr. Nagchoudhury (5) Mr. H.N. Sethna, and (6) Dr. R.

Earnings (April-Sept. 1965)

Pilot Plants	: Rs. 58,875-68
Misc. Sales	: Rs. 1,24,512-33

	1,83,388-01

11. NEW APPOINTMENTS/RESIGNATIONS

List attached.

12. FOREIGN DEPUTATIONS/AWARDS/DEGREES/HONOURS/NOMINATIONS/SPECIAL TRAINING RECEIVED AND SUMMER SCHOOLS ATTENDED :a) Foreign deputations :

On the invitation of the West German Academic Exchange Service, Prof. K. Venkataraman visited West Germany for a period of 3 weeks from 29th May 1965 to 13th June 1965.

Shri S.P. Mukherjee proceeded to France under Indo-French agreement for 2 years from June 1965, for training in the field of Chemical Engineering.

Dr. S.C. Bhattacharyya visited USSR for 4 weeks (from 29-6-65) under Indo-Soviet Cultural Programme. He delivered lectures at various universities and research institutes in the USSR.

Dr. C.G. Joshi proceeded to Geneva for 6 months (from 2-8-65) under United Nations Technical Assistance Board for studies in laboratory techniques in the field of narcotics.

Shri S.H. Iqbal proceeded to University of Caen, France, (from 12-8-65) for 9 months for training in the Chemistry of titanium compounds under the French Govt. scholarship.

Dr. S.L. Kapur visited Czechoslovakia to attend international symposia on (i) Chemistry of macromolecules and (ii) Organosilicons held at Prague. At the invitation of the university of Mainz, West Germany, he visited few manufacturers and delivered lectures at various polymer research centres in West Germany.

b) Awards and Honours

Dr. S.C. Bhattacharyya	S.S. Bhatnagar Memorial Award 1962 (Chemical Sciences)
Dr. B.D. Tilak	S.S. Bhatnagar Memorial Award 1963 (Chemical Sciences).
Dr. Sukh Dev	S.S. Bhatnagar Memorial Award 1964 (Chemical Sciences).
Dr. S.C. Bhattacharyya	Sc. D. from Cambridge University, U.K.

c) Degrees

Mr. U.N. Upadhyaya	Ph.D.	Poona University
Mr. V.D. Deo	M.Sc.(Tech)	Bombay University
Mr. N. A. Bhat	M.Sc.	-Do-
Mr. T.C. Joseph	Ph.D.	Poona University
Mr. V.K. Dhekne	Ph.D.	Bombay University
Mr. J. Lobo	M.Sc.	Poona University
Mr. A.C. Ranade	M.Sc.	Bombay University
Mr. H.V. Keer	M.Sc.	-Do-
Mrs. Parimala Jose	Ph.D.	Poona University
Mr. A.F. Mascarenhas	M.Sc.	-Do-
Miss B.M. Sayagavar	M.Sc.	Bombay -Do-
Mr. U.R. Kantak	M.Sc.	Poona -Do-

d) Nominations

Dr. S.L. Kapur	i) Member of Productivity Council, of printing industry; (ii) Member of panel of advisers to the Director, ILRI, Ranchi; (iii) Member of research and extra-service Committee of Rubber Board of India (iv) Member of Research Advisory Committee, SASMIRA.	
Dr. S.C. Bhattacharyya	Ordinary Fellow of National Institute of Science of India.	
Dr. A.P.B. Sinha	Member of Chemistry Board, AEE, Bombay.	
Dr. J.L. Bose	i) Member of Central Cotton Committee ii) Member of panel of experts, ATIRA, Ahmedabad.	
Dr. B.D. Tilak	i) Coopted on the Board of Studies in Chemical Technology, Technology Faculty, Bombay Univ. ii) Appointed Director of IDPL, HAL, HOC.	

e) Special training/Summer School

Mr. D.D. Kelkar	Documentation	INSDOC & Pub.Divn. CSIR, New Delhi.
Mr. A.S. Narula	Course of process and system control	IIT, Kanpur.

Dr. P.M. Nair	Summer school on magnetic resonance and solid state physics.	Nainital
Dr. K.P. Sinha		
Miss C.R. Daryanani	Summer school on biochemistry	Bangalore
Dr. P.N. Rangachari	Summer school on microbiology.	Pantnagar
Dr. M.C. Srinivasan		
Mr. S.R. Modak		
Mr. V.K. Bhalla		
Mrs. S. Chandra	Summer school on physics & chemistry of macromolecules.	Udaipur.
Mr. S. Gundiah		
Mr. L.C. Anand		
Dr. A.B. Biswas		
Dr. A.P.B. Sinha	Summer meeting, Computer Society of India.	TIFR, Bombay
Mr. S.N. Balasubramanian	Summer school on chemical engineering.	RRL, Hyderabad
Mr. Siskovic		
Mr. A.D. Deshpande		
Mr. A.W. Joshi	Summer school on recent trends in theoretical physics.	Bangalore
Mr. B.S. Krishnamurthy		

f) Following are the Indian universities for which NCL is the recognised centre for post-graduate work :

Punjab	Agra
Poona	Karnatak
Bombay	Vikram
Banaras	Andhra
Madras	

g) Following are the staff members who are recognised guides for different universities :

Prof. K. Venkataraman	Dr. B.D. Tilak
Dr. J. Gupta	Dr. A.B. Biswas
Dr. K.P. Sinha	Dr. H.B. Mathur
Dr. A. Goswami	Dr. (Miss) S.B. Kulkarni
Dr. L.M. Pant	Dr. A.P.B. Sinha
Dr. V.V. Dadape	Dr. D.N. Sen
Dr. P.R. Subbaraman	Dr. Sukh Dev
Dr. J.L. Bose	Dr. P.M. Nair
Dr. N.L. Dutta	Dr. C.R. Narayanan
Dr. S.C. Bhattacharyya	Dr. K.K. Chakravarti
Dr. G.R. Kelkar	Dr. A.S. Rao
Dr. V. Jagannathan	Dr. P.K. Bhattacharyya
Dr. M.R.R. Rao	Dr. S.L. Kapur
Dr. N.D. Ghatge	Dr. N. Krishnaswamy

13. AID UNDER U.N. SPECIAL FUND, COLOMBO PLAN, PL-480 ETC.

Work on investigation of the synthesis and properties of new type glycol monoalkyl ethers for the control of water evaporation to extend the industrial utilisation of cotton seed oil under PL-480 sponsored scheme. - n i l -

Chemical and thermodynamic properties of refractory materials under PL-480 Rs. 2,00,000/-

Investigation of the effect of heat on Tung oil and derivatives of tung oil and the characterisation and identification of compounds resulting from heat treatment to extend the utilisation of Tung oil under PL-480 - n i l -

14. EXPERTS

Nil.

New Appointments

<u>S.No.</u>	<u>Name</u>	<u>Designation</u>	<u>Date of appointment</u>
1.	Mr. K. Ganapathy.	SSA	28-5-65
2.	Mr. C.E. Deshpande	JSA	-do-
3.	Mr. P.N. Chaudhary	JSA	29-5-65
4.	Mr. O.W. Dias	JSA	-do-
5.	Mr. V.V. Kulkarni	JSA	22-6-65
6.	Mr. A. David	JLA	27-6-65
7.	Mr. H.V. Patel	SSA	1-7-65
8.	Mr. K.J. Rao	Sci. 'B'	1-7-65
9.	Mr. A.S. Surve	JSA	2-7-65
10.	Mr. J. Kumar	SSA	2-7-65
11.	Mr. J.K. Khullar	SSA	2-7-65
12.	Mr. S.K. Gupta	SSA	3-7-65
13.	Mr. Om Prakasha	SSA	8-7-65
14.	Mr. V. Srinivasan	SSA	-do-
15.	Miss. R.V. Bakre	JSA	19-7-65
16.	Miss. P.T. Bhople	SLA	21-7-65
17.	Mr. I. Balkrishnana	JSA	22-7-65
18.	Dr. N.R. Ayyangar	Sci. 'B'	24-7-65
19.	Mr. K.K. Chopra	Sec. Officer.	26-7-65
20.	Mr. D.R.V. Ramanan	Pur. Officer.	4-8-65
21.	Dr. B.D. Tilak	Jt. Director	5-8-65
22.	Mr. V.N. Iyer	Sci. 'B'	8-9-65
23.	Mr. V.V. Bhat	SLA	23-8-65
24.	Mr. S.R. Padalkar	Grd. Apprentice	12-8-65
25.	Mr. B.M. Sawant	SLA	23-8-65
26.	Mr. S.S. Kale	SLA	23-8-65
27.	Mr. A.T. Bhat	SLA	23-8-65
28.	Mr. P.K. Trama	SLA	24-8-65
29.	Mr. A.P. Budhkar	SLA	-do-
30.	Mr. S.P. Mahadik	SLA	-do-

33.	Miss. N.D. Ghatge	SLA	24-8-65
34.	Mr. S.D. Govitrikar	SLA	25-8-65
35.	Miss. N.B. Parkhi	SLA	27-8-65
36.	Mr. R.B. Sagde	Grd. Apprentice	27-8-65
37.	Mr. R.B. Gujarathi	SLA	31-8-65
38.	Mr. G. Samuel	SLA	1-9-65
39.	Miss. S.B. Kanade	SLA	-do-
40.	Mr. M.B. Sabne	SLA	7-9-65
41.	Mr. C.B. Rao	SLA	7-9-65
42.	Mr. B.K. Sonawane	SLA	8-9-65
43.	Miss. L.V. Shirole	SLA	9-9-65
44.	Mr. M.S. Joshi	SLA	-do-
45.	Mr. V.K. Kulkarni	SLA	-do-
46.	Mr. K. Cherian	SLA	-do-
47.	Mr. D.S. Shendekar	JLA	-do-
48.	Mr. S.G. Joshi	JLA	10-9-65
49.	Mr. K.F. Lunkad	SLA	10-9-65
50.	Mr. C. Bhaskar	SLA	10-9-65
51.	Mr. Y.D. Kulkarni	JLA	13-9-65
52.	Mr. J.K. Lulla	Mechanic	-do-

Resignations

1.	Mrs. P.V. Nijampurkar	JSA	1-5-65
2.	Dr. P.S. Rao	Pool Officer	13-5-65
3.	Mr. O.P. Shukla	SSA	10-6-65
4.	Dr. (Miss) Raj Mathur	Pool Officer	11-6-65
5.	Dr. G. Narsimhan	Sci.	28-6-65
6.	Dr. N.B. Desai	Pool Officer	30-6-65
7.	Mr. S.Y. Phansalkar	Inst. Technician	1-7-65
8.	Miss. S. Rangaswamy	JSA	21-7-65
9.	Dr. R.N. Mukherjee	Pool Officer	24-7-65
10.	Mr. D. Sugavanam	JSA	26-7-65
11.	Mr. R.M. Kumar	SSA	26-7-65
12.	Mr. D.J. Lakhani	Ref. Engineer	29-7-65
13.	Dr. S.K. Dhar	Pool Officer	31-7-65
14.	Mr. V.V. Kulkarni	JSA	21-9-65
15.	Dr. V.B. Tare	Pool Officer	27-9-65
16.	Mr. T.S. Santhanakrishnan	SSA	

33. Miss. N.D. Ghatge	SLA	24-8-65
34. Mr. S.D. Govitrikar	SLA	25-8-65
35. Miss. N.B. Parkhi	SLA	27-8-65
36. Mr. R.B. Sagde	Grd. Apprentice	27-8-65
37. Mr. R.B. Gujarathi	SLA	31-8-65
38. Mr. G. Samuel	SLA	1-9-65
39. Miss. S.B. Kanade	SLA	-do-
40. Mr. M.B. Sabne	SLA	7-9-65
41. Mr. C.B. Rao	SLA	7-9-65
42. Mr. B.K. Sonawane	SLA	8-9-65
43. Miss. L.V. Shirole	SLA	9-9-65
44. Mr. M.S. Joshi	SLA	-do-
45. Mr. V.K. Kulkarni	SLA	-do-
46. Mr. K. Cherian	SLA	-do-
47. Mr. D.S. Shendekar	JLA	-do-
48. Mr. S.G. Joshi	JLA	10-9-65
49. Mr. K.F. Lunkad	SLA	10-9-65
50. Mr. C. Bhaskar	SLA	10-9-65
51. Mr. Y.D. Kulkarni	JLA	13-9-65
52. Mr. J.K. Lulla	Mechanic	-do-

Resignations

1. Mrs. P.V. Nijampurkar	JSA	1-5-65
2. Dr. P.S. Rao	Pool Officer	13-5-65
3. Mr. O.P. Shukla	SSA	10-6-65
4. Dr. (Miss) Raj Mathur	Pool Officer	11-6-65
5. Dr. G. Narsimhan	Sci.	28-6-65
6. Dr. N.B. Desai	Pool Officer	30-6-65
7. Mr. S.Y. Phansalkar	Inst. Technician	1-7-65
8. Miss. S. Rangaswamy	JSA	21-7-65
9. Dr. R.N. Mukherjee	Pool Officer	24-7-65
10. Mr. D. Sugavanam	JSA	26-7-65
11. Mr. R.M. Kumar	SSA	26-7-65
12. Mr. D.J. Lakhani	Ref. Engineer	29-7-65
13. Dr. S.K. Dhar	Pool Officer	31-7-65
14. Mr. V.V. Kulkarni	JSA	21-9-65
15. Dr. V.B. Tare	Pool Officer	27-9-65
16. Mr. T.S. Santhanakrishnan	SSA	30-9-65
17. Mr. T.C. Joseph	SSA	-do-