ANNUAL REPORT

1965-66

NATIONAL CHEMICAL LABORATORY
POONA

NATIONAL CHEMICAL LABORATORY
POONA

1965 - 1966

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

CONTENTS

INTRODUCTION

SPONSORED PROJECTS

PRIVATE PARTIES :

1. Acriflavine 1
2. Benzoic acid 1
3. Calcium hypophosphite and phosphoric acid .. 1
4. Diethyl-m-aminophenol 1
5. Isolation of emetine from Ipecac roots 2
6. Investigation of a fermentation problem .. 2
7. Improvements in the process for the manufacture of 1-menthol from dementholised peppermint oil .. 2
8. Nonyl phenol 2
9. Pine oil from Indian turpentine oil 3
10. Sodium cyclamate 3
11. Sorbide nitrate : Sulphacetamide sodium and carbimazole 3
12. Reactive dyes 3
13. Vat dyestuffs 3

CENTRAL AND STATE GOVERNMENT INSTITUTES :

1. Composite drug research scheme on Indian medicinal plants 4
2. Commercial uses of Punjab costus (kuth) roots .. 4
3. Fabrication of electron diffraction camera ... 5
4. Constitution of lac 5
5. Lac dye 5
6. Production of titanium tetrachloride from ilmenite .. 6

PL-480 *SCHEMES*

1. Chemical and thermodynamic properties of refractory materials at high temperatures .. 7
2. Work on investigations on the synthesis and properties of new type glycol monoalkyl ethers for the control of water evaporation to extend the industrial utilisation of cotton seed oil .. 7
3. Investigation of the effect of heat on Tung oil and derivatives of Tung oil and the chracterisation and identification of compounds resulting from heat treatment to extend the utilisation of Tung oil 8

PILOT PLANTS

1. Aniline 10
2. BON acid (carbonation of phenols) 10
3. Chlorination of ethylene 10
4. Dimethylaniline 11
5. Dissolving pulp 11
6. Fine chemicals 12

RESEARCH PROJECTS

P. 1 THEORETICAL INVESTIGATIONS ON SOLID STATE AND MOLECULAR PHYSICS 14

1.1 Phonon-magnon interactions in magnetically ordered solids 14
1.2 Interactions involving conduction electrons in magnetic metals and alloys .. 14
1.3 Superconductivity in metals and alloys .. 15
1.4 Vibronic interaction in ferro– and anti-ferroelectric crystals 16
1.5 Mobility in polar semiconductors .. 16
1.6 Electronic structure of molecules 17
1.7 State of atoms in the presence of crystal and radiation fields 17

P. 2 MATERIALS FOR SOLID STATE DEVICES

2.1 Ferromagnetic materials 18

2.2 Dielectric and ferroelectric materials .. 19

2.3 Structural and dielectric studies of ferroelectric materials 19 19

2.4 Photoconductors 19

2.5 Manganites 20

2.6 Semiconducting perovskite-type materials .. 20

2.7 Oxidic semiconductors 20

2.8 Covalent semiconductors (silicon) .. 22

2.9 Electrical and thermal properties of semiconductors 22

2.10 Europium laser materials 22

2.11 Properties of metal-insulator-metal junctions .. 23

P.3 THIN FILMS 24

3.1 Structure of thin films 24

3.2 Physics of thin films 25

P.4 CRYSTAL AND MOLECULAR STRUCTURES

4.1 Crystallography 26

4.2 Spectrochemical studies 27

P.5 THERMODYNAMIC AND KINETIC STUDIES .. 29

5.1 Low temperature calorimetry 29

5.2 High temperature calorimetry 30

5.3 Thermodynamic properties of coordination compounds 30

5.4 High temperature solid-gas-reactions and diffusion in solid state 31

5.5 Oxidation behaviour of metals and alloys .. 31

5.6 Thermodynamic properties of solutions .. 32

P.6 NUCLEAR AND RADIATION CHEMISTRY .. 32

6.1 Mössbauer spectra of spinel-type compounds ... 32

6.2 Mössbauer effect in oxidation-reduction system 34
6.3 Radiation effect on materials 34

P.7 CATALYSIS 34

P.8 SYNTHETIC INORGANIC CHEMISTRY .. ..

8.1 Titanium organics 36
8.2 Diphenyl dithiophosphinic acid complexes with metals 38
8.3 Coordination compounds, their semi-aromaticity and isomerism 38
8.4 Coordination polymers 39
8.5 Infrared studies of coordination compounds ... 40
8.6 Phosphors 41
8.7 Chromatographic adsorbents 41
8.8 Fluorine chemicals 41

P.9 PHYSICO ANALYTICAL CHEMISTRY 42
9.1 Analytical service 42
9.2 New methods of analysis 43
9.3 Mechanism of the molybdate dimethyl glyoxime reaction 43
9.4 Direct reduction of insoluble vat dyes in the solid state at the dropping mercury electrode 43

P.10 NATURAL ORGANIC PRODUCTS .. ...

10.1 Oleoresins and resinoids 44
10.2 Wood extractives 44
10.3 Hamycin 44
10.4 Carbohydrates 45
10.5 Utilisation of groundnut shells 45
10.6 Medicinal plants 46
10.7 Essential oils 47
10.8 Plant pigments 52

P.11 SYNTHETIC ORGANIC CHEMISTRY

11.1 Studies in synthetic dyes 53
11.2 Synthetic drugs 57
11.3 Steroids 59
11.4 Synthetic carbohydrates 60
11.5 Transformations and synthesis in terpenoid series 61
11.6 Macrocylic musk compounds 64
11.7 Oxidation of alkyl side-chains in aromatic compounds 65
11.8 Diethyl-m-toluamide 65
11.9 Sorbic acid 65

P.12 PHYSICAL ORGANIC CHEMISTRY

12.1 NMR studies 65
12.2 Mills-Nixon effect and allied problems .. 68
12.3 Mass spectrometry 68
12.4 Polyesters as stationary phases in GLC analysis 68

P.13 MICROBIOLOGY

13.1 National collection of industrial micro-organisms 69
13.2 Microbiological oxidation of hydrocarbons .. 69
13.3 Metabolism of C_5—dicarboxylic acid ... 69
13.4 Bacterial diastase 70
13.5 Microbiological transformations of terpenes ... 70

P.14 GROWTH OF PLANT CELLS 74

P.15 ENZYMES

15.1 Hexokinase 75
15.2 Phytase 76
15.3 Acetylcholinesterase 76
15.4 Brain DPNase 76

15.5 Nitrate and nitrite reductase 77
15.6 Citrate-oxaloacetate lyase 77
15.7 ∝–Amino acid acylases 78

P.16 PHYSICO-CHEMICAL STUDIES OF POLYMERS

16.1 Solution properties of polymers 78
16.2 Stereospecific polymerization 79
16.3 Telomerization 80
16.4 Polymerization of turpentine fractions .. 80
16.5 Degradation of long chain molecules by ultrasonics 80

P.17 ION EXCHANGE RESINS

17.1 Improved styrene-DVB cation-exchange resin .. 81
17.2 Styrene-DVB anion-exchange resins .. 81
17.3 Electrodialysis with ion-exchange membranes .. 82
17.4 Preparation of porous ion-exchange resins ... 82
17.5 Column studies on cation and anion-exchange resins 82
17.6 Catalysis by ion-exchange resins .. 82

P. 18 INDUSTRIAL POLYMERS

18.1 Polystyrene foams 83
18.2 Rigid sand filters 83
18.3 Polyurethanes 83

P. 19 SURFACE COATINGS

19.1 Styrenated alkyds 84
19.2 Linseed oil emulsion 84
19.3 Chemical modification of lac 84
19.4 Coating for steel tapes 85

P. 20 RUBBER

20.1 Modified rubber 85
20.2 Rubberised cork sheets 85

20.3 Sponge textiles 86
20.4 Rubber chemicals 86
20.5 Rubber base sealants 86

P. 21 GRAFTING ON CELLULOSE 86

P. 22 PROCESS DEVELOPMENT

22.1 Vitamin B_6 87
22.2 Vitamin C 87
22.3 Acetanilide 87
22.4 Phthalates (Dioctyl and Dibutyl) .. 88

P. 23 PROCESS DESIGNS 88

P. 24 CHEMICAL ENGINEERING STUDIES

24.1 Latent heats of vaporization 89
24.2 Prandtl number of organic liquids .. 89
24.3 Dependence of fluidized bed characteristics on relative pressure drops in the grid and the bed 89
24.4 Thermodynamics, kinetics and reactor designs .. 90
24.5 Mass transfer 91

P. 25 MISCELLANEOUS WORK

25.1 Foundry chemicals 92
25.2 Television radio suppression ignition cable .. 92
25.3 Preparation of catalyst grade nickel formate .. 92
25.4 2, 4-Dinitro resorsinol and mono-nitro resorcinol 93
25.5 Preparation of biochemicals 93
25.6 Recovery of mercury 93
25.7 Utilisation of bauxite sludge 93

APPENDICES

A. I Processes in production 94

A. II Processes released and awaiting production .. 95

A. III Processes on which technical know-how has been developed .. 96

A. IV Projects completed during 1965-66 .. 97

A. V Services rendered to outside parties .. 97

A. VI Demonstrations 99

A. VII Training 100

A. VIII Technical services 100

A. IX Special fabrications 100

A. X Seminars and Lectures 101

A. XI Symposia 102

A. XII Staff news 102

A. XIII Publications 106

A. XIV Indian Patents in force 119

INTRODUCTION

The National Chemical Laboratory is now entering its seventeenth year. A report of the work carried out during 1950-60 has been published earlier and a report for the period 1960-65 is under publication. So far, the annual reports of the laboratory were only cyclostyled for a limited circulation. Starting with the present report, annual reports will be published regularly in the future for wider circulation.

Seventeen of the processes developed by the laboratory are already in production by the licencees and twentyeight more processes have been released to industries, and are awaiting production. On other twentyseven more processes, details have been obtained and these are under evaluation.

The laboratory is making a determined effort to reorient its research programme towards applied, time–targetted, projects of immediate significance to the industry. The use of modern management techniques, such as Programme Evaluation Review Technique (PERT) for time–targetting and scheduling applied work, has been recently introduced. Twenty two sponsored schemes are in progress of which thirteen are sponsored by industry. Five sponsored projects have been concluded during the year.

Of the 7 pilot plant projects, work on BON acid and dimethylaniline have been concluded and the scheme on titanium tetrachoride has now been sponsored by industry. Work on rubberised cork sheets, styrene-DVB anion exchange resins, and design of a prototype vapour phase chromatograph unit have been successfully concluded and it is hoped that industry will shortly take over these projects for commercial production.

During the year under review, collaboration with project engineering firms has been sought with a view to offer turn-key plants based on NCL know-how, for acetanilide, dibutyl and dioctyl phthalates. It is hoped that by adopting this procedure the industrial utilisation of know-how, developed in the NCL, will be expedited.

Being a discipline oriented laboratory, due emphasis is also laid on basic work, to provide the essential foundation of applied research. During the year 114 papers have been published and 17 read at various symposia. The Laboratory organized a symposium on " Chemistry of terpenoids " in collaboration with the National Institute of Sciences and the Kurukshetra University in June 1965. The symposium was largely attended by scientists from India and abroad.

A brief resume of the highlights of the research projects in progress is given in the report.

SPONSORED PROJECTS

PRIVATE PARTIES

1. *Acriflavine*

Acriflavine is an important antiseptic used in general medical practice. 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 system.

2. *Benzoic acid*

Benzoic acid is an important aromatic fine chemical and has variety of uses in pharmaceutical and other industries. Work has been undertaken for the optimisation of the operating conditions for the liquid phase catalytic oxidation of toluene to benzoic acid. Laboratory scale trials have been completed and a pilot plant of 10 kg/hour capacity is being erected.

3. *Calcium hypophosphite and phosphoric acid*

Development of process know-how for pharmaceutical grade calcium hypophosphite has been undertaken. A unit for 30 kg/day of calcium hypophosphite will be designed for the sponsor.

A pilot plant to treat 1 kg of phosphorous per batch has been set up. Calcium hypophosphite in solution, insoluble calcium phosphite and a gaseous mixture of phosphine, diphosphine and hydrogen are obtained in the process. The reaction conditions have been standardised in the pilot plant.

A burner has been developed to oxidize the above phosphine to phosphorous pentoxide by burning it in air. The recovery of phosphoric acid obtained from the combustion products of phosphine is being improved.

4. *Diethyl — m — aminophenol*

This is an important intermediate required for the production of certain basic dyes. Optimum conditions for the technical preparation of the chemical from ethyl chloride and metanilic acid have been obtained on a 4 kg./batch scale. The final project report is being prepared for the sponsor.

5. *Isolation of emetine from Ipecac roots*

The principal constituent of the non-phenolic fraction of the total alkaloids of the roots of *Cephaelis ipecacuanha* is emetine. Cephaeline which is also present in the alkaloid is too toxic for use and hence is usually converted to emetine. Emetine is a white amorphous powder sparingly soluble in water and readily soluble in alcohol. The principal therapeutic use of emetine is in the treatment of amoebiasis. Emetine is generally injected subcutaneously or intramuscularly in the form of hydrochloride. Optimum conditions for the isolation of emetine and conversion of cephaeline to emetine, are being worked out.

6. *Investigation of a fermentation problem*

The work was sponsored to investigate the causes of spoilage of some of the Ayurvedic pharmaceutical preparations obtained by fermentation. We have carried out some laboratory investigations and will be suggesting them suitable preventive measures.

7. *Improvements in the process for the manufacture of l-menthol from dementholised Peppermint oil*

A 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 on examination indicated that theoretically the oil can yield 68% l-menthol from l-menthol and l-menthone present in the oil.

A number of experiments have been carried out to standardise the process of reduction of l-menthone to l-menthol. A stereospecific method of reduction of l-menthone to l-menthol has been worked out. This method appears to be superior to the method now being used by the firm and has been demonstrated to the chemical engineers of the firm.

A specification for dementholised peppermint oil is also being drawn up by the Indian Standards Institution and the necessary scientific data have been collected in this connection.

8. *Nonyl phenol*

Nonyl phenol is a potential raw material for the preparation of ethylence oxide condensates which are finding increasing applications as surface active agents. The development of a process for the technical preparation of the chemical from propylene trimer and phenol by using acid catalyst has been undertaken.

9. *Pine oil from Indian turpentine oil*

Commercial samples of pine oil manufactured by the party have been systematically analysed and different constituents present in the oil have been characterised.

10. *Sodium cyclamate*

Sodium cyclohexylsulfamate or sodium cyclamate is used as a non-nutritive sweeting agent in different types of food and beverage preparations. It is about 30 times as sweet as sucrose. The preparation is being attempted from cyclohexylamine.

11. *Sorbide nitrate : Sulphacetamide sodium and Carbimazole*

All these are pharmceutical chemicals used in the treatment of different ailments. Sorbide nitrate taken orally relieves pain in the heart. Sulphacetamide sodium is used in the treatment of acute conjunctivities, infections after injuries or burns, in the form of solution or ointment. Carbimazole is an anti-thyroid substance. It is reputed to cause less hiperplasia and vascularity of the gland, than other anti-thyroid agents.

Optimum conditions for the technical preparations of the above pharmaceuticals are being worked out.

12. *Reactive dyes*

Reactive dyes react with the cellulose fibre resulting in a chemical bond. These dyes are cheaper and have better all round fastness properties than conventional type.

Several new reactive dyes derived from cyanuric chloride have been synthesised and samples have been sent to the sponsor for evaluation and testing.

13. *Vat dyestuffs* (Golden yellow GK)

Experimental conditions to prepare Golden Yellow GK from naphthalene and benzoyl chloride have been optimised on a 2 kg /batch scale. Pilot plant trials in a 5 gal. reactor have been successfully carried out. A new and simple process for the manufacture of benzoyl chloride has also been developed.

The final product was sent to the sponsor for evaluation. On their approval of the product, a detailed project report has been submitted.

CENTRAL AND STATE GOVERNMENT INSTITUTES

1. *Composite drug research scheme on Indian medicinal plants*

(Ministry of Health, Govt. of India)

Work on the following three plants has been started.

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

Punarnava : Air-dried powdered roots have been subjected to successive extraction with different solvents. Thin layer chromatography of these extracts shows them to be complex mixtures. One crystalline compound m. p. 136-7° isolated from petroleum ether extract, has been identified as β — sitosterol.

Shatavari : Dried roots have been extracted successively by different solvents. From n-hexane extract a crystalline compound m. p. 153-56° has been isolated. It is most probably α_2- sitosterol. Two crystalline compounds have also been obtained from ether extract. The ethyl acetate extract and ethanol extract consist mostly of glycosides and carbohydrates and they are under investigation.

Putikaranja : Thin layer chromatography of different solvent extracts of the powdered kernel of the mature seeds shows presence of a number of closely related compounds. Benzene and chloroform extracts are found to be quite similar. A number of a pure crystalline compounds which are different from the previously reported α, β and γ -caesalpins, have been isolated and are being characterised.

Different extracts from all the above materials have been sent for pharmacological tests.

2. *Commercial uses of Punjab Costus (Kuth) roots*

(Govt. of Punjab)

To find out ways for profitable utilisation of the costus roots grown in Lahaul and Spiti areas of Punjab, a large number of samples of roots grown under various manurial and irrigational trials supplied by the Govt. of Punjab have been examined for yield of oil and lactones.

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

3. *Fabrication of Electron Diffraction Camera*

Work on the fabrication of electron diffraction cameras, one for Gauhti University and one for Fertiliser Corporation of India, Sindri, is nearing completion.

Order for one more camera for the Defence Science Laboratory, Delhi has been accepted.

4. *Constitution of Lac*

(Indian Lac Research Institute, Ranchi)

Although lac is well known as a versatile natural resin used in different industries, little is known about the constitution of the resin molecule. Such a knowledge is likely to open new fields for lac utilisation.

Number of acids arising from the hydrolysis of lac, namely jalaric, shellolic, epishellolic, laksholic, epilaksholic, butolic and aleuritic have been isolated. The structures of jalaric, laksholic and epilaksholic were established for the first time. Results obtained strongly suggest that the chief building blocks of lac resin are aleuritic acid and jalaric acid.

The work relating to the determination of structure of lac molecule involves isolation of pure fraction of the resin and systematic degradation of the pure fraction, which may reveal the mode of linkages between aleuritic and jalaric acids.

The isolation of pure fraction using repeated precipitations has been successfully completed. The major products formed during the oxidative degradation of the pure fraction have been isolated and a good progress has been made in their structure elucidation by chemical and spectroscopic methods.

5. *Lac dye*

(Indian Lac Cess Committee, Ranchi)

The colouring matter of lac is under investigation. There are possibilities of using lac dye as a food colour.

Erythrolaccin : The synthesis of erythrolaccin (*Tetrahedron Letters* No. 1, 33, 1965) by an unambiguous method has been completed.

Laccaic acids : Part of the results so far obtained has been published.[44] 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 chromtography on polycaprolactam powder. The complete structure of one laccaic acid not containing nitrogen has been determined, and extensive data, which should shortly lead to the complete structure of a nitrogen-contating lac pigment, have been obtained.

In connection with the NMR spectra of the nitrogen-containing laccaic acid, several model compounds such as some derivatives of $N\ \beta$-hydroxyethyl-anthranilic acid are being synthesised.

The action of BF_3-etherate and acetic anhydride on methoxy-anthraquinones 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 understudy 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.

6. *Production of titanium tetrachloride from ilmenite*

(M/s Travancore Titanium Products Ltd., Trivendrum)

Ilmenite deposits of India are large and are in a concentrated form on the coastal line of Kerala and Kanyakumari. In recent years substantial deposits of ilmenite have also been found on the Ratnagiri coast line of Maharashtra. Presently the sponsoring firm is manufacturing Titanium dioxide pigment from ilmenite by the conventional sulphate process. Besides that the titania obtained by this process is not very pure and is of anatase form, the process requires substantial quantities of sulphur, which India has to import.

A more modern process for the direct production of pigment grade rutile titania is known as the chloride process, wherein titanium dioxide is obtained by burning the titanium tertachloride in oxygen. In the sulphate process, the titanium dioxide is produced by employing rutile titania seed prepared from titanium tetrachloride.

During this sponsored scheme, the data from earlier developed process for the chlorination of enriched ilmenite has been employed in the work on the present pilot plant. After a series of successful trials on 2 kg./hour of titanium tetrachloride plant, a 10 kg./hour pilot plant has been fabricated and installed. The unit includes special arrangements for charging hot briquetted, enriched material to the reactor and discharging the ash from bottom.

PL-480 SCHEMES

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

(National Bureau of Standards, Washington)

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

Equilibrium reactions at high temperatures in the metal metal halide systems ($Al + AlCl_3$ and $Mn\text{-}Mn\ Cl_2$) are also being studied to determine the heats of formation of the monohalides and their chemical reactions. The equilibrium reaction :

$2Al\ (1) + AlCl_{3\,(g)} \rightleftarrows 3\ AlCl_{(g)}$ between 1125° and 1425°K yielded the heat of reaction $\triangle\ Hr_{1275} = 90{\cdot}86 \pm 1{\cdot}6$ Kcal. The entropy $\triangle\ Sr_{1275}$ was $60{\cdot}12 \pm 1{\cdot}3$ Cal. degree^{-1}.

The equilibrium reaction of $AlCl_{(gas)}$ and $MgO_{(crystal)}$ between 1298° and 1465°K was found to be $4MgO_{(c)} + 3AlCl_{(g)} \rightleftarrows MgAl_2O_{4(c)} + AlCl_{3(g)} + 3\ Mg_{(g)}$.

It yielded a value for third law heat $\triangle H_{298} = 22{\cdot}21 \pm 1{\cdot}01$ K cal mole^{-1}, which gave — $553{\cdot}29 \pm 2{\cdot}09$K cal mole^{-1} for the heat of formation of magnesium aluminate from the elements.

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

(U. S. Department of Agriculture, Washington)

Water evaporation from lakes and reservoir is a dominant problem especially for countries in arid and semi-arid zones. Amongst the various attempts being made for conservation of water, the use of monolayers of long chain alcohols and alkoxy ethanols seems to be promising method to reduce evaporation losses of water.

Work on the project is divided into two aspects :

(i) *Preparation of cetosteryl alcohol mixtures* : Preparation of saturated alcohols by hydro-genolysis of cotton seed oil was continued. Experimental conditions for obtaining more than 90% conversion have been worked out. These experiments have been extended to various other oils viz. groundnut, cocoanut and castor.

(ii) *Properties of mono-layers : Evaporimeter studies :* A number of alcohol mixtures obtained in hydrogenolysis experiments were tested on evaporimeters and their efficiency as water evaporation retardants was evaluated. It was found that these alcohol mixtures a show better water evaporation retardation as compared to pure cetyl and stearyl alcohols.

Surface viscosity : Surface viscosities of C_{16}, C_{18}, and C_{20} C_{22} alcohols were measured for various shear rates and pressures at different temperatures, using a rotational viscometer. These data will be used for evaluating intermolecular interactions and dimensional phase changes in different films.

Specific resistance to evaporation : Specific resistance to evaporation has been measured for a number of long chain alcohols and alkoxy ethanols as a function of film pressure in a Langmuir trough at room temperature. The results obtained show that with the increase in chain length and surface pressure, the specific resistance (γ) increases. The (γ) values for alkoxy ethanols have been found higher than the corresponding alcohols. Mixed monolayers of alcohols and alkoxy ethanols showed higher γ values at low pressures($\sim$ 15 dynes/cm) than the individual components. With increase in the ethylene oxide substitution in the polar group, the specific resistance values deteriorated, mono condensates exhibiting highest γ values.

3. *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*

(U. S. Department of Agriculture, Washington)

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

Accordingly, the fundamental changes in the formation of the cyclic monomer and dimer resulting from the heat treatment of oil are being investigated.

Pure samples of methyl α-and β-eleostearates were prepared by esterification of pure α-and β-eleostearic acids respectively, by ethereal diazomethane. Methanolysis of tung oil was found simple and convenient for the large scale preparation of methyleleostearate. Cyclization of methyl α-or β-eleostearates by thermal energy alone was found unsatisfactory. A variety of substances have been tested for their catalytic activity for this selective isomerisation, and a few useful catalysts discovered.

Mild thermal treatment (at 160° for five hours) of methyl eleosterate in presence of a catalyst resulted in a 30% conversion to the cyclic monomer. Chromatographic and spectral studies of the cyclic monomer revealed that the monomer is formed *via* the initial isomerised triene with the 11-double bond cis-configurated. Isolation of this unique isomer of eleostearate has been reported for the first time. The characterisation of this central triene compound has been achieved by the new modified technique of chromatography i. e. the inverted dry column chromatography over $AgNO_3$- silica gel.

The dimer fraction (yield 10%) isolated in the mild thermal treatment for methyl α – eleostearate was investigated by different chromatographic techniques. Two liquid compounds have been isolated in pure form which surprisingly displayed almost indistinguishable IR, UV and NMR spectra. It appears that these two dimers are stereo-isomers.

◆ ◆ ◆

PILOT PLANTS

1. *Aniline*

Aniline is an important organic chemical required in large quantities in the dyestuff and other chemical industries. A process has been developed for the vapour phase catalytic hydrogenation of nitrobenzene to aniline. Based on the kinetic data and process conditions obtained on a laboratory scale, a pilot plant utilising a multi-tubular fixed bed reactor with 2 kg. / hour capacity was successfully run with 97% conversion per pass. Engineering data on the pilot plant are being collected.

2. *BON acid* (carbonation of phenols)

BON acid is an important intermediate used in the manufacture of arylamide (Naphthol AS series) which have vastly extended the scope of azoic colours.

Two processes are known for the preparation of BON acid by the action of carbon dioxide on alkali naphtholates : (i) dry process, and (ii) wet process. The wet process offers certain mechanical advantages. This process has been successfully worked out on a 2-3 kg. / batch scale, and it has been found that the reaction can be completed in less time than in the dry process.

The present licensed capacity of 960 T/year is reported to be adequate for internal consumption. However, a few dye manufacturing firms have shown interest in our process in order to be independent of other firms manufacturing BON acid. This demand is expected to be of the order of 80 T/year. Accordingly design data for a 80 T/year plant have been collected.

Attempts are being made to reuse the β-naphthol produced in the reaction without further purification. Preliminary trials have shown promising results.

The carbonation technique using the wet process is also being applied to the carbonation of phenol and cresols.

3. *Chlorination of ethylene*

Trichloroethylene, perchloroethylene and other chlorinated products of ethane and ethylene are extensively used as solvents. The estimated requirements of trichloroethylene by 1970 is about 15,000 T/year. Its most important application is in vapour degreasing of metals. Perchloroethylene is used in the drycleaning of garments.

In industry symmetrical tertrachloroethane is obtained by chlorination of acetylene and trichloroethylene is obtained by dehydrochlorination of tetrachloroethane. A series of experiments on direct chlorination of ethylene was carried out in 2″ glass reactors at different temperatures and space velocities using an active carbon catalyst. The main constituents of the resultant product were 30-35% tetrachloroethylene and 40% of trichloroethylene, which could be isolated by fractional distillation. Work is in progress to increase the selectivity for trichloroethylene.

Ethyl chloride is an intermediate in the manufacture of tetraethyl lead and ethyl cellulose. The estimated demand for ethyl chloride in 1970 is about 300 T/year. This project also includes process development for ethyl chloride by chlorination of ethane to produce ethyl chloride and HCl, the hydrochloric acid obtained in this reaction being utilised for the hydrochlorination of ethylene. Work has been commenced on the second step.

4. *Dimethylaniline*

This is an important intermediate for dyestuffs. Current Indian requirements are estimated at 600 T/year, which are presently met by imports.

Pilot plant trials on the pressure reaction of methanol and aniline were conducted in an autoclave in which 8-10 kg. of dimethylaniline per batch could be produced. An yield of over 95% (based on aniline) was obtained for a 99·5 % pure product.

Based on the pilot plant data obtained, the design of a 600 T/year plant has been prepared and passed on to a project engineering firm for preparing a turn key design for release to industry.

5. *Dissolving pulp*

The indigenous capacity for producing rayon grade pulp from bamboo is limited, and considerable quantities of the pulp have to be still imported causing yearly drain of about Rs. 4 crores of foreign exchange.

Pilot plant investigations on various indigenous cellulosic raw materials for the manufacture of dissolving grade pulps were undertaken and are in progress. A two-stage alkaline pulping process, based on removal of pentosans by alkaline liquors, was developed to give a 90-97% α-cellulose containing less than 5% pentosan from *D. strictus* and *B. arundinacea.* Except for the slightly higher iron content the pulp possesses all other properties such as reactivity, filtrability of the viscous solution, tensile strength and elongation of the filament yarn etc. within the desired range.

Pilot plant trials on pulping of groundnut shells by water-prehydrolysis sulphate process gave unbleached pulp (yield 30-32%) with 3% pentosan. The bleached pulp has the following chemical analysis :

α – cellulose – 88 to 90%; Pentosan – 2·2 to 2·7%; D. P. – 510–550; Ash – 0·24 to 0·4%.

As these pulps could not be converted to sheets due to their small fibre length, a method for the manufacture of carboxymethyl cellulose (CMC) from the wet pulp was developed. According to a consumer's report the CMC so prepared can be employed for limited uses.

Melocanna-bamboo species was investigated as per suggestion of Director of Industries, Tripura, by different pulping methods. Acid-prehydrolysis-sulphate and two-stage alkaline pulping processes are both suitable for this species. The latter pulp contains 95·4% α cellulose, 0·15% ash, 95 p. p.m. silica, 42 p. p. m. iron and 3·5 to 4·5% pentosan.

Pilot plant trials on *B. arundinacea* by 7·5 and 27·5% Na_2O in the first and the second stage at 160 to 170° gave a pulp with 4·49% pentosan, 6.8 to 11 Cp, unbleached viscosity and about 37.5% yield. Preliminary investigation on *petalladinum, strobilanthus* and 51 mixed hard wood species from Maharashtra State indicated promising results. Acid-prehydrolysis-sulphate pulping of *Eucalyptus hybrid* to obtain pulp less than 1% pentosan and 97-98% α—cellulose by hot and cold alkaline purification has been under taken.

6. *Fine chemicals*

The small scale production of different fine chemicals required by scientific workers in research laboratories and speciality chemicals required by industry and defence was started in the National Chemical Laboratory through this project in April 1964. During the last two years, its activities have been considerably stepped up and are fulfilling a vital purpose of national importance in stimulating the progress of chemistry in the country. The chemicals prepared by the group are those which were almost entirely imported hitherto, and hence the production is resulting in the saving of considerable foreign exchange.

More than 300 fine chemicals are now routinely manufactured by the unit. During the year under report, following are some of the new special chemicals introduced : p-Benzoyloxybenzaldehyde; Allantoin; Mono-nitro resorcinol, 2-4-Dinitro resorcinol; Tri-nitro resorcinol; 1-Acetyl naphthalene; 5-Amino barbeturic acid; Azobenzene; Fluorobenzene; Fluorotoluene etc.

On having received consistent orders from different parties, the group has now started the regular manufacture of the following chemicals : Phenoxyacetic acid; Chromatographic alumina and silica gel (for thin layer and column chromatography); Anhydrous aluminium chloride; Titanium tetrachloride; Silicon tetrachloride; Costus root oil; Macrocyclic perfumery compounds; Malonic acid.

◆ ◆ ◆

RESEARCH PROJECTS

P-1 THEORETICAL INVESTIGATIONS ON SOLID STATE AND MOLECULAR PHYSICS

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. Based on these, experimental work is also undertaken to develop suitable devices having appropriate physical properties.

1.1 *Phonon-magnon interactions in magnetically ordered solids*

Most of the thermodynamic and transport properties of magnetic solids are governed by the low-lying elementary excitations in the system and their mutual interaction. In the low temperature region, the important elementary excitations are magnons (quanta of spin wave) and phonons (quanta of lattice wave). Atomistic theory of the interaction processes involving phonons and magnons in ferro–, antiferro and ferri-magnetic crystals were developed. The mechanisms of energy exchange between spin and lattice systems were clearly dilineated and they were in agreement with observed results for the three types of magnetic crystals.

Based on the above studies the thermal conductivity of ferrimagnetic solids has been completed. It is found that the thermal conductivity in the low temperature region is governed by the scattering of phonons by magnons, mass defects and strain fields and boundaries of systems. The contribution of magnons is significant in the temperature region 5° to 15°K. The theoretical calculations when compared with the experimental results on manganese ferrite ($MnFe_2 0_4$) and magnetic garnets ($Y_3 Fe_2 Fe_3 0_{12}$) show good agreement[2].

The green function technique was applied for the study of the energy spectrum of the quasi-particles and the magnetization in two-sub-lattice ferrimagnets. Results obtained for the energy and magnetization agree well with those obtained by the conventional spin-wave method.

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

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 metals and alloys containing transition elements. This gave processes of the type A $[S_c^x S_d^x + S_c^y S_d^y]$ 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 the form given below.

$$-\sum_{(l,m)} \frac{V^2_{sd} J_{sd}}{\hbar^4 / (2m^*)^2} \frac{V^2}{N^2} 16\pi^2 k_F^2 \left[\frac{\pi}{2} e^{-\lambda x} \frac{\cos x}{x^3 (1+\lambda^2)} - \frac{\cos^2 x}{x^4 (1+\lambda^2)^2} \right.$$

$$\left. - \frac{\pi}{2} e^{-\lambda x} \frac{\sin x}{x^4 (1+\lambda^2)} \left(1 - \frac{2}{1+\lambda^2} \right) + \cdots \right] S_1 \cdot S_m \ldots\ldots$$

This has an oscillatory behaviour with distance. This mechanism conforms with the magnetic behaviour of some Heusler alloys[25].

1.3 *Superconductivity in metals and alloys*

It is well known that superconductors with high transition temperatures (T_c) will open up numerous avenues for practical applications. With this in view, various physical factors which influence the transition temperature of superconductors were studied. The two important factors studied were the effects of pressure (P) and impurity.

A microscopic theory was developed which takes into account the fact that owing to external pressure a modulation in the crystal and impurity potentials is brought about. The resulting perturbation gives rise to interband and intraband transition of conduction electrons. The theory predicts a relation

$$Tc^{(p)} = a - bP + cP^2 \qquad (1)$$

$$\text{or } Tc^{(p)} = a + cP^2 \qquad (2)$$

depending on the values of the parameters a, b, c. involved. This explains the decrease of $T_c^{(p)}$ with pressure (cf. equation-1) and under certain condition the likely increase of $T_c^{(p)}$ with P (cf. equation-2). These predictions are in agreement with a large body of experimental results[23].

The effect of impurities of transition elements in various superconductors has been of great interest in recent years. It is found that impurities having magnetic moments decrease the transition temperature whereas those which do not have net magnetic moment increase the transition temperature of superconductors. The latter phenomenon has been explained by formulating a new attractive mechanism between a pair of electrons responsible for superconductivity. The process arises from Coulomb and exchange interactions between the electrons via localised impurity states below and above the Fermi surface. The predicted increase in transition temperature has the form:—

$$\left[\frac{\Delta\, Tc}{Tc^{(o)}} = A\,\xi + B\,\xi^2\right]$$

where ξ is the impurity concentration and A and B parameters of the theory. This explains the observed increase of transition temperature in superconducting alloys viz. titanium containing iron.

1.4 *Vibronic interaction in ferro- and anti-ferro electric crystals*

The ferroelectric crystals are of great technical importance in various solid state devices. However, the basic mechanism by which a dielectric solid undergoes a phase transition to the ordered face has not been understood clearly. The present work invokes the role of electron—vibration coupling for elementary units in these materials. It is shown that the low lying electronic states of the unit Ti-O-Ti or TiO_6 in barium titanate crystals couple with odd vibration mode to give rise to instability of the transverse optical mode. This provides the required microscopic description of the ferroelectric phase transition. Higher order anaharmonic terms stabilise the soft mode beyond a certain temperature. The effective frequency has the following form :—

$$W^2_{\text{eff}}\,(0) = T - Tc$$

$$Tc = \left(\frac{A^2_{g,u}}{10_{g,u}1} + \nu - W^2_u\right) / \beta \qquad \text{where}$$

$A_{g,u}$ is the matrix element which connects states $|\, g>$ and $|\, u>$; $J_{g,u}$ is their energy separation and β, ν are constant. This is in agreement with observed behaviour[12].

1.5 *Mobility in polar semiconductors*

The transport properties of semiconductors are governed by the interaction of carriers of current (electrons and holes) with various other physical factors in the system such as phonons and static perturbing potentials. A general theory of mobility in compound semiconductors has been completed and a new concept of multi-band conduction has been introduced. This involves intra-band transition effects which are achieved by optical phonon scattering or perturbations due to alloy effect. The former when coupled with acoustical phonon scattering gives rise to two phonon processes and the mobility (μ) temperature dependent relation[13].

$$\mu = \mu_0{}^{\circ}\, T^{-\frac{5}{2}}$$

On the other hand, the alloy effect and the acoustical phonon scattering gives

$$\mu = \mu_0^s \, T^{-\frac{3}{2}}$$

The total mobility (μt) inclusive of both the situations is described by the general relation

$$\mu \text{ Total} = \frac{\mu_0^{(s)} \mu_0^{(o)} T^{-\frac{5}{2}}}{\mu_0^{o} T^{-1} + \mu_0^{(s)}}$$

For $\mu_0^{(o)} T^{-1} >> \mu_0^{(s)}$ This reduces to

$\mu_1 = \mu_0^{(s)} T^{-\frac{3}{2}}$ and for

$\mu_0^{(o)} T^{-1} << \mu_0^{(s)}$, one gets $\mu_T = \mu_0^{(o)} T^{-\frac{5}{2}}$

The high and low temperature behaviour in most of the compound semiconductors is explained by above equations. Also the observed concentration dependence follows the following expression[24].

$$\mu o^{(s)} = \frac{c}{a + b \quad \Sigma f_r f_s |F_{rs}|^2}$$

where f_r f_s etc. are the concentrations of components. a, b, c $|F_{rs}|$ are appropriate parameters.

1.6 *Electronic structure of molecules*

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

For the derivatives of hydrocarbons such as quinones, the δ function potential was introduced. Using such perturbations the wave functions and the electron densities of the above mentioned chemicals have been obtained. This work satisfactorily explains the optical behaviour and the electrophillic and nucleophillic substitution patterns in case of many conjugated organic compounds[26].

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

The idea is to study the spin and electronic states of paramagnetic atoms in crystals 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.

The spin phonon interaction in paramagnetic systems have been taken into account. By a suitable canonical transformation one gets spin-spin interaction in these systems. Such processes are important for relaxation phenomenon of paramagnetic systems.

P. 2 MATERIALS FOR SOLID STATE DEVICES

2.1 *Ferromagnetic materials*

During the last ten years, a new class of permanent magnet material, commonly known as hard ferrite, has been developed in other countries. These compounds are isomorphous with $Pb\,Fe_{12}\,O_{19}$ (magnetoplumbite) and have a high uniaxial anisotropy and a high coercive force. A number of new ferrites such as silver-lanthanum, thallium-lanthanum etc., have been synthesised and the effect of impurities and preparative conditions in case of many other known ferrites have been studied. By a proper choice of composition, preparation conditions and doping agents, it has been possible to get a $(B \times H)$ max of $1{\cdot}7 - 1{\cdot}8 \times 10^6$ gauss-oersted for un-oriented samples of barium ferrite. This figure is higher than that obtained elsewhere for any material of this class. Ferrimagnetic compounds of the type $BaMe_2Fe_{16}0_{27}$ have been prepared where Fe^{3+} is replaced by Ca^{2+} and Si^{4+} and Me^{2+} stands for Zn^{2+}, and Fe^{2+}. The magnetic properties of these compounds are under investigation.

Soft ferrite materials which have high electrical resistivity have been developed abroad for high frequency use and are finding increasing applications in radio, television, radar etc. Nickel-zinc ferrite is widely used for making antenna rods for radios. In order to avoid use of imported nickel in the above type of ferrites, a new type of magnesium-zinc ferrite, with a certain proportion of other soft ferrites as impurity, has been developed, the performance of which is comparable with nickel-zinc ferrite. The reaction temperature, sintering temperature and their durations have been fixed on the basis of various experiments. The saturation magnetization, permeability and Q-factor have been studied. Large scale preparations and extrusion of antenna rods are being undertaken. Similar studies on lithium-zinc ferrite are being carried out.

Magnesium-manganese ferrites suitable for microwave applications have also been synthesised.

New lead-lanthanum ferromagnetic oxides isomorphous with perovskite have been synthesised and their structure and saturation magnetisation determined.

2.2 *Dielectric and ferroelectric materials*

The study of dielectric and ferroelectric properties of the compositions in the system $[Ba_xPb_{(1-x-y/2)}Nb_yZr_{1-y}O_s]$ has been completed.

To study the existence of surface charge layers a polarising and recording system has been fabricated. The values of spontaneous polarisation arising due to space charge layers were calculated from the transient current characteristics of the samples.

The piezoelectric coupling coefficients of polarised samples have been measured by a modified oscillometric detector constructed in the laboratory. The set up comprises of a variable frequency oscillator, audio detector and amplifier. Kr values of some compositions investigated have been found to be higher than those reported for conventional P-Z-T materials.

2.3 *Structural and dielectric studies of ferroelectric materials*

The investigation is 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 wider applications of their properties can be made.

Work was continued on the measurement of spontaneous polarization, dielectric constant and curie point for doped lead titanate samples of the general formula $Pb(La_{\frac{1}{2}}V_{\frac{1}{2}})_x Ti_{1-x}0_3$, changing the value of x by 0·05 for different compositions. Preliminary studies showed that spontaneous polarization completely vanished with the samples made with x greater than 0·3. Consequently only six samples were made in this range for the study. It is observed that the value of spontaneous polarization at room temperature increases as the value of x increases, reaches maximum when x becomes 0·2 and there after decreases. The dielectric constant also changes in a similar way. Only two compositions with x = 0·15 and 0·2 show sharp curie temperature at 170° and 100° and high dielectric constant of 692 and 793 respectively. The values have been estimated from measurements made on several different samples of a particular composition. Further work on powder X-ray diffraction study for these samples is being carried out.

2.4 *Photoconductors*

A detailed study of preparatory conditions on the photoconductivity properties of PbS and CdSe films has been made. Chemically deposited and vacuum deposited films of PbS were prepared. During the chemical deposition, the effects of the incorporation of some chemical oxidants in the bath were investigated. The results obtained were encouraging and systematic investigation of conditions for preparing films with controlled oxidant concentration are being tried. Substantial quantities of various sulfides and selenides were prepared to be subsequently used for the preparation of thin films by vacuum deposition of the individual compound and solid solutions.

The photosensitive layers of CdSe have been prepared by vacuum deposition techniques and their spectral response, photosensitivity and decay characteristics are being investigated.

A system for studying the photosensitivity using chopped radiation has been set up and the fast response time under square wave excitation is being measured.

2.5 *Manganites*

Several mixed oxidic spinels containing Cu^{++} and Mn^{+++} have been prepared for the study of their crystallographic and electrical properties. The measurements of electrical resistivity in the temperature range 25-800° of the following systems have been completed : (1) $Co_xCu_{1-x}(Mn_2)0_4$ (2) $Mg_xCu_{1-x}(Mn_2)0_4$ (3) $CuMn(MnNi)0_4$

2.6 *Semiconducting perovskite-type materials*

Contact characteristics of different materials were studied to find the most suitable contact for doped semiconducting barium titanate materials. Indium amalgam was found to give the best results. Number of samples were prepared by conventional ceramic techniques and were sintered at 1250 to 1300°. The resistive and dielectric properties of these semiconducting materials are being studied with the help of a newly constructed electronic bridge.

2.7 *Oxidic semiconductors*

It has been found that the semiconductivity of certain oxidic compounds is controlled by the chemisorption of gases on its surface and a correlation between the surface conductivity and its catalytic activity has been observed.

Large plate-like zinc oxide single crystals have been grown by a method developed in the laboratory. The electrical conductivity has been studied as a function of temperature and oxygen pressure. A similar study has been carried out on thin films of zinc oxide prepared by evaporating zinc in vacuum and then oxidizing it in air. On plotting log R against 1/T, a minimum and a maximum in resistance is observed at 200° and 400° respectively. Thin films of In doped ZnO (n type) has lower resistances and at high indium concentration the extrema in the resistance disappears completely. Similar studies have been carried out in hydrogen and nitrogen and it has been found that the resistance follows the following order :

$$^{R}\text{ZnO}\,(H_2) < {}^{R}\text{ZnO}\,(N_2) < {}^{R}\text{ZnO}\,(\text{air})$$

High conductivity in nitrogen has been attributed to the ionization of zinc interstitials (activation energy 0·05 ev). In the presence of oxygen, adsorbed oxygen on the surface acts as traps and decrease the concentration of electron. The resistivity in presence of oxygen is therefore higher than that in nitrogen. In hydrogen atmosphere, the electron concentration is further increased due to creation of excess zinc interstitials which ionize to give electrons. The extrema have been attributed to the presence of two types of adsorbed oxygen ions.

Conductivity changes of the plate-type crystals have also been studied in vacuum. Similar studies have been carried out on polycrystalline zinc oxide pellets and the results compared with those described above. In all these cases the conductivity is governed by changes in the surface.

On the other hand, in the case of rod-type single crystals where the surface area is relatively smaller, the bulk conductivity is predominant. It has been observed that in the temperature range of 25-200° they exhibit n-type conductivity (activation energy of 0·02 ev), while at 200-600° the conductivity changes to p-type (activation energy 0·92 ev). This change has been attributed to ionization 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 of the compound shows an absorption edge at 390 mμ, corresponding to a band gap of 3·24 ev.

These zinc oxide single crystals have been irradiated in air at different temperatures by γ-rays obtained from a Co^{60} source. The resistance first increases with irradiation time, reaches a maximum after about 5 hours, decreases slightly and finally attains a constant value. At 100° the maximum in the resistance appears earlier while at 300° it vanishes completely. This behaviour has been attributed to the change from n-type to p-type conduction due to the adsorption of oxygen. The effect of ambient atmospheres has also been studied. In nitrogen atmosphere the resistance decreases with irradiation time which supports the above conclusion. In case of irradiation in presence of hydrogen, the resistance initially decreases, then starts increasing and finally becomes constant. This has been attributed to the reduction and subsequent precipitation of zinc as a separate phase.

In the studies on crystallographic and electrical properties of $FeCuMn0_4$, $CuCrMn0_4$ and $NiMnCr0_4$, it has been found that these 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.

2.8 *Covalent semiconductors* (silicon)

A unit for the preparation of silicon tetrachloride (capacity 1/2 kg. of $SiCl_4$/hour) from ferro-silicon was run continuously and the product was sold through FCP. Purification of this silicon tetrachloride has been achieved to give a starting material for the preparation of semiconductor grade silicon. An apparatus for the apitaxial growth of silicon by the reduction of silicon tetrachloride vapour with pure hydrogen has been successfully worked out. The deposit of silicon takes place on a substrate maintained at 1100-1200° by induction heating. With the help of semiconductor grade silicon so prepared, some p-n junction devices are being tried.

2.9 *Electrical and thermal properties of semiconductors*

The thermoelectric figure of merit (Z) of a material is given by $Z = \frac{\alpha^2}{K\rho}$

where α is the thermoelectric power, K is the thermal conductivity and ρ is the resistivity.

In order to increase the efficiency of the system, some physical agencies which will increase α and decrease K and ρ have to be introduced. Since magnetic impurities (as shown by the theoretical studies, p.13) interact with both phonons and electrons, experimental studies with thermoelectric semiconductors doped with paramagnetic impurities have been undertaken.

Measurements on gadolinium doped with bismuth telluride show a very high figure of merit, at 82°K at a certain concentration region. The low value of resistance is due to spin-dependent scattering of carriers which has a negative contribution in a certain temperature region.

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 increase of concentration upto 0·16 atomic % 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 $Bi_{2\cdot2}Pb_{0\cdot78}Te_{4\cdot02}$ has a cubic structure and shows good thermoelectric properties.

2.10 *Europium laser materials*

Materials in which population inversion of electrons can be obtained by optical pumping or other means are known to be useful laser materials.

Recently much interest has been shown in rare earth chelates particularly Eu^{3+} chelates which show laser action.

Number of new europium chelates viz. (a) mixed ligand complexes containing β–diketone and the acetate anion, (b) β–diketonates complexed with nitrogen donors and (c) β-diketonates complexed with Lewis bases, have been prepared for their possible applications as laser materials

The chemical and spectroscopic properties of these materials are being investigated. Absorption and fluorescence spectra of these compounds have already been studied from room temperature down to liquid nitrogen temperature in various solvents. The absorption spectra of these compounds show a very broad band in the UV region which is the characteristic absorption of the organic part of the molecules. The excitation is transferred to the Eu^{3+} ion intramolecularly. The fluorescence spectrum and energy levels of Eu^{3+} in these compounds have also been investigated. Their fluorescence spectra have been recorded on a Cary Model 14 spectrophotometer using the fluorescence attachment at Indian Institute of Technology, Kanpur (Dept. of Physics). The fresh solutions ($\sim 10^{-5}$M) have been examined in a 20 mm. quartz cell immersed in liquid nitrogen in a transparent quartz dewar, and irradiated with mercury vapour lamp using suitable filters. It is observed that the Eu^{3+} fluorescence is composed of several narrow lines which involve emissions from excited level to $^5D_0$ the terminal states of emissions $^7F_0$, $^7F_4$ and $^7F_2$. Out of all the transitions observed, the $^5D_0 \rightarrow {}^7F_2$ transition which is supposed to lase, is very intense and has a sufficiently narrow band width. In fact the intensity of this fluorescence in some of the compounds prepared is higher than in compounds in which laser action has been observed elsewhere.

Many factors are required to be considered while evaluating a material for laser applications, e. g. quantum yield, the radiative life time, spectral band width etc. and these properties are being studied.

2.11 *Properties of metal-insulator-metal junctions*

Although insulators are known to be bad conductors of electricity, it has been observed that under certain conditions, a large amount of current can be drawn through thin films of insulators. The current transport phenomenon in these insulating films has opened a very promising field in view of its application in thin film tunnel diodes, field effect transistors, negative resistance devices etc.

The metal insulator metal sandwitches using Al, Bi, Cd, Zn, Au, In etc., as electrode metal films and their oxide or sulphide films as insulators have been studied. The ohomic contact (In-CdS) generally gave space charge limited current in thick films. The non-ohomic contact to perfect insulator (Al-Al_2O_3) gives tunneling in very thin films (∠100 Å) and in thicker films Schottky-type conduction is predominent. To ensure the mechanism, the voltage current characteristic has been studied at different temperatures and at different insulator film thicknesses. In certain cases (CdS and ZnS), the effect of light has also been studied.

During this study a negative resistance phenomenon has been observed. This has applications in solid state switching devices. The mechanism of negative resistance is not yet fully known and hence studies have been undertaken to explore this mechanism in CdS, Al_2O_3 and ZnS thin film structures. The results obtained show that avalanche break-down double injection of carriers may be one of the possible mechanisms responsible.

Some of the organic compounds such as pongomol, curcumin etc., have been used as insulating materials. They show a voltage controlled negative resistance.

P. 3 THIN FILMS

It is well known that materials in thin film state behave quite differently from those in the bulk state. Some phenomena such as catalytic activity, adsorption, thermionic emission, superconductivity etc., are characteristics of surface layers only. Even many metals behave as semiconductors when they are in thin film state. In view of the great technological importance of semiconductors in various fields, fundamental studies on structure and physics of thin films have been undertaken.

3.1 *Structure of thin films*

Electron diffraction studies have been made on the vacuum deposited films of selenides and tellurides of zinc, cadmium and bismuth and also of crystal growth process, phase transformation with temperature. It has been found that ZnSe, ZnTe, CdSe and CdTe 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 oriented, 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 deposit and the substrate etc. The formation of hexagonal phase with the cubic 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. $\{1\bar{0}11\} + \{20\bar{2}3\}$ 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, $a_o = 3{\cdot}06$ A° and Bi_2Te_3, $a_o = 3{\cdot}25$ A°). These deposits also grow epitaxially on the different faces of rock salts. Bi_2Se_3 film, however, on prolong heating decomposes to BiSe ($a_o = 5{\cdot}99$ A°) growing epitaxially on the (100), (110) and (111) faces of rock-salt with a strong tendency to develop facets.

Studies have also been made on the structures and epitaxial growth of chalkogenides, intermetallic compounds and metalloids such as HgSe, HgTe, InSe, InSb, InTe, SnSe and SnTe from the vapour phase at different substrate temperature etc, in vacuo. Many new phases which were otherwise absent in bulk structure were found to develop in thin film state.

Saw-tooth wave generators developed previously in the laboratory for spreading of the diffraction spots into rectangular or square areas have been 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.

3·2 *Physics of thin films*

A systematic study of semiconducting properties of thin films of PbS, PbSe, PbTe, Bi_2Se_3, Bi_2Te_3 and InSb of varying thicknesses has been made and the measurements of semiconducting parameters are standardized for the first time. Effects of factors such as thickness, rate of evaporation, substrate temperature on the 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 control thin film properties in the same way as impurities in the bulk are established.

For all materials studied the resistivity (ρ) decreased with increase of thickness and finally becoming nearly constant with greater thickness. The rate of evaporation considerably affected the shape of the curve. Resistivity *vs* 1/T curve for both PbS and PbSe showed considerable adsorption phenomenon. PbTe films did not, however, show any adsorption effect. The energy band gap in case of PbS, PbSe and PbTe respectively varied from 1·2 to 1·6 eV, 0·7 to 0·9 eV and 0·22 to 0·44 eV for various film thickness, thinner films giving higher values. The thermoelectric power (α) varied similarly with thickness, ranging from 150 to 375 UV/°C 340 to 450 UV/°C and 300 to 400 UV/°C respectively near about room temperature. For PbS and PbSe films thermoelectric power (α) gradually rose to a maximum value and then dropped steeply to zero with the increase of temperature and again increasing with a negative sign with the further rise of temperature. Cooling also showed similar effects, though the path did not exactly fall on the heating curve. These films were predominantly ' p ' type when deposited and then changed to ' n ' type with the increase of temperature of the surrounding. The mean free path (*l*) for all compounds was found to be of the order of 10^{-5} cm, which was considerably less than the film thickness used. The carrier concentration calculated from Hall effect, resistivity and thermoelectric power measurements, was of the order of 10^{17}cm^{-3}, whereas the last method gave 10^{18} cm^{-3}. TCR was negative and the value showed a gradual decrease with the increase of temperature and rising again, after passing through a minimum value.

In the case of Bi_2Se_3, the log R *vs* 1/T curve changed the shape continuously depending on the maximum temperature of heating. This appears to be linked with the change of structure. Further, these films were always ' n ' type irrespective of the maximum temperature of heating. Bi_2Te_3, on the other hand, did not show any such peculiarity. The thermoelectric power of the former was only of the order of 6×10^1 to 8×10^1 UV/°C, whereas the latter was about $1{\cdot}8 \times 10^2$ UV/°C. It was noticed that the thermoelectric power for the Bi_2Se_3, films was not depending on the maximum heating temperature.

Investigations on the Hall coefficient (R_H) of various film thicknesses ranging between 2,000 to 50,000 A° are carried out with respect to thickness, dimensional ratio (*l*/b) annealing and the substrate temperature. R_H was 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, raised, R_H value.[116]

Further, it was found that the deposit formed at higher substrate temperature showed increase in conductivity as well as mobility. This was found to to be due to the decrease in the number of carrier concentration in the deposited film as a result of higher substrate temperature, thus in effect, increasing the purity of deposited film.

P. 4 CRYSTAL AND MOLECULAR STRUCTURES

4.1 *Crystallography*

Crystallographic studies of compounds reveal the molecular geometry and the nature of the intra and inter-molecular linkages and thus provide valuable basic data for understanding the mechanism of physico-chemical behaviour of material systems.

Studies have been undertaken on para-nitrobenzoic acid, ortho-nitrobenzoic acid, 3,5-dichloroanthranilic acid, benzoyl glycine and para-bromobenzoyl glycine, in order to correlate their structures with physical and chemical properties.

Para–nitrobenzoic acid crystallizes in the monoclinic system with $a = 12{\cdot}97$, $b = 5{\cdot}07$, $c = 21{\cdot}43$ A; $\beta = 96{\cdot}4°$, Z = 8 and space group, A2/a. The structure was refined with the help of about 600 general reflexions and bond lengths have been obtained with an accuracy of about ±0·01 A.

The structure analysis of orthonitrobenzoic acid, using about 700 general reflexions is nearing completion. It crystallizes in the triclinic system, space group $P\bar{1}$ with 2 molecules per unit cell of dimensions.

$$a = 7{\cdot}55, \quad b = 4{\cdot}99, \quad c = 12{\cdot}50\text{ A};$$
$$\alpha = 122{\cdot}5°, \quad \beta = 95{\cdot}3°, \quad \gamma = 108{\cdot}9°.$$

The Fourier maps show considerable distortion of the molecule from planarity, presumably due to intramolecular overcrowding.

3,5–Dichloro-anthranilic acid crystallizes in the monoclinic system, group $P\frac{2}{a}$ with 4 molecules per unit cell of dimensions.

$$a = 12{\cdot}44, \quad b = 17{\cdot}10, \quad c = 3{\cdot}78, \quad \beta = 93°.$$

The approximate structure has been obtained and the refinement is in progress. Preliminary work on the structure of benzoyl glycine and para-bromobenzoyl glycine has been undertaken.

Refinement of the structures of (1) sodium 2-oxovalerate, and (2) sodium 2-oxoheptylate by three dimensional least square methods is in progress. The trial structure of (3) sodium 2-oxocaproiate ($a = 39{\cdot}46$, $b = 6{\cdot}11$, $c = 5{\cdot}94$ A° and space group $Iba\,2$) has been obtained.

A theoretical study has been made of diffuse X-ray scattering from neutron irradiated graphite. The results agree with the experiments of Bacon & Warren 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.

4.2 *Spectrochemical studies*

Infrared and electronic spectral studies are used in the elucidation of molecular structural problems as well as in the quantitative analysis of compounds. The spectral data collected are interpreted to characterise the compounds and correlate with their physical and chemical properties.

Studies on the infrared spectra of long chain alkoxy ethanols were extended to compounds $CH_3(CH_2)_{17}(OCH_2CH_2)_2OH$, $CH_3(CH_2)_{17}(OCH_2CH_2)_3OH$ and $CH_3(CH_2)_{21}(OCH_2CH_2)_2OH$ in the solid and liquid states. These compounds were found to show considerable supercooling tendency. Odd chain alkoxy ethanols containing 17 and 19 carbon atoms have been synthesised. The spectra of these two compounds indicated the presence of both the *trans*-and *gauche* configuration in the solid state and only the *gauche* form in the liquid state similar to the even chain compounds, but unlike the corresponding normal alcohols. The spectra of short chain ethylene glycol, cellosolves, carbitol, diethers of ethylene glycols and diethylene glycol at low temperature have been investigated, and their rotational isomerism is found quite dissimilar to the long chain compounds. A low temperature cell has been constructed and used for studying the IR spectra at liquid nitrogen temperature.

Infrared spectra of salicylaldoxime, its deuterated analogue, oximino-benzoyl and acetyl salicylaldoximes, salicylaldoxime diacetates are investigated in solution to establish the hydrogen bonding properties of the oximino and phenolic hydroxyl groups. It has been found that O–H...N hydrogen bond is weaker than O–H...O bond which is contrary to the normal behaviour.

In continuation of the studies on substituted acetylurea $RCH_2 \cdot CONH\,CONH \cdot R_1$ certain deuterated analogues have been prepared and their IR spectra investigated. Contrary to the general expectations, compounds with $R_1 = H$ and $R =$ phenyl, phenoxyl, p-chlorophenoxyl have the imide NH *cis* to both the carbonyl groups, while in the compounds with R_1, other than hydrogen, the NH is *trans* to the carbonyls. The various amide and imide group vibrations have also been assigned by the help of the deuteration studies.

Infrared spectra of N-acetyl, N-benzoyl and p-bromo–N-benzoyl-glycines, their deuterated analogues and potassium salts have been studied. Non-dimeric structure for N-benzoyl glycine and dimeric structure for p-bromo-N-benzoyl glycines have been proposed on the basis of the COOH group frequencies. The spectra of divalent Cu, Co, Ni, Mn and Zn complexes in the hydrate, anhydrous and deuterated forms are being interpreted.

Visible spectra of Co(II)N-acetyl and N-benzoyl glycinates in dimethyl sulphoxide and dimethyl formamide indicated the formation of tetrahedrally coordinated complexes having a structure like $Co(DMSO)_2(BGl)_2$ and containing a large anion like BGl (N-benzoyl glycinate).

The infrared spectral investigation of the three amino benzoic acid showed that the meta-isomer alone exists in the zwitter ion form in the solid state though in solutions of chloroform and dioxan the normal form has been found. With the help of the deuterated meta-amino benzoic acid, their potassium salts and hydrochlorides, complete assignment for the meta-amino benzoic acid has been carried out.

The isomeric benzene amino sulphonic acids have also been investigated and it has been found that all the three of them exist in zwitter ion form in the solid state. Complete assignments of the three amino sulphonic acids are being carried out by the spectral analysis of the hydrochloride, potassium salt and their deuterated compounds.

The complexes of the orthanilic acid with Cu, Co, Ni, Mn and Cd have been prepared and the nature of the complexes are being investigated by spectro-chemical analysis.

Magnetic susceptibilities of Cu (II), Co (II), Ni (II) and Mn (II) complexes with lactic, malonic, mandelic, tartaric, maleic and fumaric acid, have been measured using Guoys method and they are found to have no unusual features, the only exception being Cu(II) mandelate.

P. 5 THERMODYNAMIC AND KINETIC STUDIES

Most of the substances exhibit drastic change in their properties on either cooling to low temperatures or heating to high temperatures. Variations of specific heat characteristics with temperature would provide an insight into the details of the molecular structure, electronic energy level pattern, and the mechanism of various transitions and phase transformations occuring in solids. Besides, it provides basic data for evaluating thermodynamic functions, especially the free energy and the equilibrium constant, which enables either to control or predict chemical behaviour.

5.1 *Low temperature calorimetry*

Recently the compounds with perovskite-like structures are becoming very important as they show many interesting solid state properties. KMF_3, where M denotes a divalent 3d transition group element such as Mn, Co, Ni and Cu, is one such series which shows antiferromagnetic ordering at low temperatures. In order to obtain information about magnetic interactions, phase transition mechanism and related thermodynamic data, heat capacities of $KMnF_3$, $KCoF_3$, $KNiF_3$ and $KCuF_3$ have been measured in the temperature range 78-300°K using an isothermal calorimeter. Anomalies in their heat capacity vs. temperature behaviour have been observed for $KMnF_3$ at 83·3° and 179·0° for $KCoF_3$ at 109·5° for $KNiF_3$ at 253·5° and for $KCuF_3$at 233·2°K. All these transitions have been identified as the antiferromagnetic paramagnetic changes except that at 179·0°K in the case of $KMnF_3$, which is attributed to a crystallographic transition. The Neel temperatures as determined from heat capacity data are, in general, in good agreement with those obtained using other techniques such as magnetic susceptibility, neutron diffraction, X-ray analysis and thermal conductivity.

Heat capacity measurements of a corresponding diamagnetic salt, $KZnF_3$, will enable to get a detailed picture of the entropy and enthalpy changes associated with the antiferromagnetic ordering in these compounds, and are now under way.

5.2 *High temperature calorimetry*

Thermodynamic investigations of a series of compounds, $SrX_{\frac{1}{2}}Y_{\frac{1}{2}}O_3$ (where X = Mo, W and Y = Ni, Co) and manganese-tellurium system have been undertaken using an adiabatic calorimeter working in the range 300-600°K. Heat capacities of $SrMo_{\frac{1}{2}}Ni_{\frac{1}{2}}O_3$ and $MnTe_2$ have been determined. The former exhibits, a hump with a maximum at about 452·0°k which is attributed to a change in the crystalline lattice from tetragonal to cubic symmetry, while the latter reveals normal behaviour. Thermal studies of $SrW_{\frac{1}{2}}Co_{\frac{1}{2}}O_3$ have been undertaken.

Thermodynamic properties such as entropy, enthalpy and free energy of all these compounds have been evaluated in the relevant temperature range.

5.3 *Thermodynamic properties of coordination compounds*

Studies on the thermodynamic properties of transition metal complexes of amino acids in aqueous solutions have been undertaken with a view to understand the nature of specificity shown by the coordinating ligands, and their radiation protection properties.

The thermodynamic quantities $\triangle F$, $\triangle H$ and $\triangle S$ have been determined for the interaction of Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} ions with amino acids serine and threonine in aqueous solutions. The experimental data show that the enthalpy changes are negative and entropy changes are positive in all cases; the order of enthalpy change is in agreement with the Irving-William order of divalent complexes. The unusual higher values of $\triangle S$ for cupric complexes is due to the Jahn-Teller distortion of the octahedral symmetry of the complexes.

The values of Ligand Field Stabilization Energy (LFSE) calculated from the thermodynamic data have been found to agree with the value of LFSE calculated from the visible and UV spectra of the complexes of Co^{2+},Ni^{3+} and Cu^{2+} ions with serine and threonine.

5.4 *High temperature solid-gas-reactions and diffusion in solid state*

There is a growing interest in the high temperature reactions in all branches of applied sciences. Studies on the nature of solid gas reactions at high temperatures have been undertaken along with the studies on intermetallic diffusion to provide data on mobility of atoms at high temperatures. Studies on oxidation kinetics of copper, lanthanum, gadolinium, and silver-indium alloys had been completed earlier by three different techniques : (i) Gulbransen type vacuum microbalance with a sensitivity of 0·2 u g/cm,^{2} (ii) differential manometers system and (iii) automatic recording volumetric apparatus at constant pressure. The results were supplemented by photomicrography.

The oxidation of dysprosium metal foils has been studied in the temperature region 500-800° 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 the growth of Dy_2O_3 through the inward diffusion of oxygen ions through the oxide layer.

The diffusion of silver in aluminium metal has been studied in the temperature interval 400-630° by means of residual rativity method with the aid of Ag^{110m}. The value of diffusion coefficient is given by the equation

$$D = 0{\cdot}073 \exp\left[\frac{-27674}{RT}\right] \text{cm}^2/\text{sec.}$$

$$Q = 27{\cdot}674 \text{ K cal/mole}$$

$$D_0 = 0{\cdot}073 \text{ cm}^2/\text{sec.}$$

5.5 *Oxidation behaviour of metals and alloys*

The oxidation of vacuum deposited lead films (~ 3000 A°) has been studied at 30 mm of Hg oxygen pressure and in the temperature range 227-307°. The kinetic behaviour of oxidation was found to be direct logarithmic at 263°, 283° and 307°. The plot of Δm (the mass of oxygen uptake by lead film/cm^2) *vs* log t (t = time of oxidation) gave two straight lines, the one for longer time having smaller slope. The initial data on oxidation of lead films in the temperature range 227-307° also fit in well with parabolic law of oxidation.

The oxidation of vacuum deposited bismuth films at ~ 30 mm of Hg oxygen pressure in the temperature range 175-250° has also been studied. The kinetic data fit in well with the parabolic law of oxidation. The oxygen uptake at different temperatures (175-250°) corresponds to a Bi/O ratio significantly greater than the calculated value of 0.66 for Bi_2O_3. This deviation from stoichiometry may be due to either oxygen deficiency or excess bismuth in Bi_2O_3. The nature of the defect structure was investigated by measuring the dependence of the electrical conductivity and transference number on the ambient oxygen partial pressure (PO_2). The conductivity (σ) was found to vary as $PO_2^{-1/6}$ in the pressure and temperature ranges 10^{-2} mm Hg to 10^2 mm at 200-317°, respectively. A deviation from this pressure dependence has been explained with the help of transference number data. The ionic and electronic transference numbers were determined by measuring the e. m. f. of the cell $Bi/Bi_2O_3/O_2^{(g)}$, Ag, at different temperatures and oxygen pressures.

5.6 *Thermodynamic properties of solutions*

The study of thermodynamic properties of solutions provide valuable information needed in design engineering.

A precision ultrasonic interferometer is being developed to find out thermodynamical data such as adiabatic compressibility, specific heat at constant volume and apparent molal properties etc.

The ultrasonic velocity of carboxy methyl cellulose solutions of various concentrations ranging from 0·1 g/dl to 5 g/dl at 25° has been measured. It is observed that sound velocity gradually rises in proportion to the concentration. The plot of specific velocity increment, ($u-u_0$) / C *vs* concentration shows a sharp maximum in the very dilute region. The shape of the curve is very similar to the viscosity *vs* concentration curve for polyelectrolyte solution.

P. 6 NUCLEAR AND RADIATION CHEMISTRY

The discovery of nuclear resonance absorption, now known as Mössbauer effect has led to its application not only in nuclear physics but also in relativity, solid state physics, chemistry, metallurgy and bio-physics.

6.1 *Mössbauer spectra of spinel type compounds*

Mössbauer spectra of cubic ferrites containing either a ferrous ion or a ferric ion and only at one type of site in the spinel structure i. e. tetrahedral (A) or octahedral (B) have been studied with the constant velocity drive apparatus in which Co^{57}/Cu source is moved with respect to absorber. It has been found that in Fe^{2+} [Cr_2^{3+}] 0_4, the tetrahedral site symmetry is non-cubic at room temperature even though the bulk symmetry as determined by x-ray is cubic. The observed quadrupole splitting of 2·70 ± 0·04 mm/sec. at —194° is due to creation of an electric field gradient (EFG) on the tetragonal distortion ($c/a < 1$) of the lattice at that temperature.

Fe^{2+} ion in Ge^{4+}, $Fe\,[Cr_2]\,O_4$ is less co-valent than in $Fe\,[Cr_2]\,O_4$ 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 $Ge^{4+}\,[\,Fe_2^{2+}\,]\,O_4$ is due to the presence of trigonal field at the B sites in the spinel structure. Confirmatory evidence is provided by the of quadrupole splitting in $Zn^{2+}\,[\,Fe_2^{3+}\,]\,O_4$ and $Cd^{2+}\,[\,Fe_2^{3+}\,]\,O_4$ which have ferric ion only at the B sites. The large value of quadrupole splitting in the Mössbauer spectra of $Ge^{4+}\,[\,Fe_2^{2+}\,]\,O_4$ as compared to that of the spectra of $Zn^{2+}\,[\,Fe_2^{3+}\,]\,O_4$ and $Cd^{2+}\,[\,Fe_2^{3+}\,]\,O_4$ is due to the fact that the Fe^{2+} is a more sensitive probe for the EFG than the ferric ion.

Table

S.No.	Absorber	Absorber *temp.	Isomer shift w. r. t. stainless steel (mm./sec.)	Quadrupole splitting (mm/sec.)	Line width (mm./sec.)
1.	$Fe^{2+}\,[\,Cr_2^{3+}\,]\,O_4$	150°	0·94±0·04	—	0·80±0·04
		120°	0·92±0·04	—	0·80±0·04
		100°	0·94±0·04	—	0·82±0·04
		25°	0·96±0·04	—	1·04±0·04
		—194°	1·18±0·04	2·70±0·04	—
2.	$Ge^{4+}\,[\,Fe_2^{3+}\,]\,O_4$	100°	1·17±0·04	2·86±0·04	—
		25°	1·20±0·04	2·80±0·04	—
		—194°	1·15±0·04	2·78±0·04	—
3.	$Zn^{2+}\,[\,Fe^{3+}\,]\,O_4$	25°	0·45±0·04	0·38±0·04	—
		—194°	0·45±0·04	0·32±0·04	—
4.	$Cd^{2+}\,[\,Fe^{3+}\,]\,O_4$	25°	0·48±0·04	0·80±0·04	—
		—194°	0·53±0·04	0·64±0·04	—

* source 25°

6.2 *Mössbauer effect in oxidation-reduction system*

Mössbauer spectra of ferrous and ferric compounds of cysteine have been studied. Ferric tricysteine prepared in nitrogen atmosphere shows only one resonance peak at —0.32 mm/sec. while the same compound when prepared in air shows three resonance peaks—0.32, 0.40 and 2·0 mm/sec. The resonance peak in the first compound and the first resonance peak in the second compound may be ascribed to be due to the presence of the ferric ion. The other two resonance peaks in the second compound may be interpreted as being due to the presence of the ferrous ion with an isomer shift of 1.54 mm/sec. and quadrupole splitting of 1.6 mm/sec. These results indicate that the catalytic oxidation of cysteine to cystine takes place through the reversible electron-transfer reaction $Fe^{2+} \overset{e}{\rightleftharpoons} Fe^{3+}$.

6.3 *Radiation effect on materials*

The possibility of the use of gamma radiations in promoting reactions of industrial importance is being explored.

The effect of temperature and metaltions Fe^{2+}, Fe^{3+}, Ag^{2+}, Uo_2^+ and Ce^{4+} on the yield of naphthol in the radiolysis of naphthalene in three different solvents (alcohol, tetrahydrofuran and acetic acid) has been determined.

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°) 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.

A preliminary investigation of the radiolytic amination of naphthalene and benzene has indicated that the formation of corresponding amines takes place with the 'G' values of 10—20. The estimation of the amines was done by UV spectra.

P.7 CATALYSIS

The programme of work on catalysis includes the following aspects : (1) Study of evaporated pure metal films so as to understand the fundamentals of catalytic action shown by different transition metals. (2) Study of physicochemical properties of catalysts and compositions of potential catalytic importance. (3) Preparation of hydrogenation catalysts and studies on hydrogenation kinetics to evaluate their activity and mechanism of reactions. (4) Preparation of vanadium pentoxide catalyst.

For the study of metal films, suitable high vacuum unit has been designed and fabricated.

The thermal decomposition behaviour of nickel formate, nickel oxalate and copper formate has been studied in the temperature range 30-800° by measuring the surface areas and densities of the decomposition products. The decomposition products have been characterised by infrared absorption and X-ray diffraction analysis.

Nickel formate shows a maximum at 250° in the plots of surface area against temperature of calcination in air. This peak is due to the decomposition and disintegration of the formate, increasing the surface area followed by partial crystallization of the oxide, which reduces the area.

Nickel oxalate shows a maximum at 350° in similar plots. This peak is observed immediately before the completion of decomposition to oxide. Ni-Cu formate shows a maximum at 200° in the plot of surface area against temperature, it is then followed by a decrease in area due to rapid bulk sintering of the oxide.

Thermogravimetric studies of the above mentioned compounds have been done in air, hydrogen and nitrogen atmospheres.

The X-ray diffraction studies of the copper-nickel alloys obtained by the dry reduction in hydrogen of their mixed carbonates at 250° for two hours showed that the change in unit cell dimensions *vs* composition deviate from the Vegard's law.

The differential thermal analysis (DTA) of the mixed nickel-copper carbonates showed overlapping peaks for dehydration and decomposition for nickel and copper components, the areas under the peaks decreasing with copper content.

Magnetic studies of the mixed nickel copper components and of the mixed oxides obtained from them by calcination at 500° for 8 hrs. have also been completed.

Further, the cause of promoter action of copper on the activity of nickel is being investigated.

Attempts are being made to make use of nickel carbonate in place of for the preparation of catalyst for hydrogenation of fatty oils nickel formate. It was found that it is not possible to prepare an active catalyst by the wet reduction of nickel carbonate, as its reduction in oil takes place above 250°. In the dry state, its reduction temperature is between 180-230°. Incorporation of some copper carbonate was found to lower the reduction temperature (160-180°) so that catalysts comparable in activity with the commercial samples could be prepared by the wet reduction of the mixed carbonates in oil at 220-240°. The selectivity of these copper promoted catalysts is also found to be good. The catalyst appears to be quite stable, as no fall in activity was detected over a long period. Optimum conditions for coprecipitation and preparation of the active catalyst have been investigated with the help of a semi-micro hydrogentation kinetics unit, specially disigned and set up for this purpose.

The commercial superiority of the silica-based vanadium pentoxide catalysts for the oxidation of sulphur dioxide is now generally accepted. In India there is only one firm manufacturing the catalyst in collaboration with a foreign firm. Though a mass of patent literature exists on this catalyst, the actual method in use by each manufacturer is still a guarded secret.

In the course of a laboratory investigation synthetic samples were developed from sodium silicate, ammonium vanadate and potassium bisulphate having high conversion efficiency at non-equilibrium space velocities. The catalyst has been produced in the form of 6 mm × 5 mm. dia. solid cylindrical pellets.

Further tests in and outside the laboratory have revealed that NCL catalyst is as good as the commercial one in many ways. However, its crushing strength is lower than usual and several factors are being studied in pelletting the catalyst powder to improve its crushing strength.

P. 8 SYNTHETIC INORGANIC CHEMISTRY

8.1 *Titanium organics*

Basic research on the synthesis and study of new titanium organics in which the organic moieties are linked to the titanium non-ionogenically through oxygen (or other) atoms has been undertaken.

Very little literature information is available on –(TiOP) – type of titanium organics. The general observation that they are often highly polymerized by co-ordination of the metal atoms from phosphoryl oxygen atoms was reported earlier. The study of the reactions of titanium tetrachloride and alkyl phosphates is further complicated by the fact that the reaction product is itself a mixture of two products in certain cases. From an unstable dichloro compound of titanium (IV), the pure oxo-compound could be isolated by cautious hydrolysis. Simpler products were obtained by taking chelated titanium dichlorides for reaction with the alkyl phosphates. For example, resorcinoyl-titanium dichloride $(C_6H_4O_2)TiCl_2$ reacted with the alkyl phosphates in dry nitrogen to give $(C_6H_4O_2)Ti[O(PO)(OR)_2]_2$ as expected (R = methyl, ethyl, n-butyl). With diacetoxy-titanium dichloride $(CH_3COO)_2TiCl_2$, however, the acetoxy groups were replaced by oxygen giving polymeric products of the composition $OTi[O(PO)(OR)_2]_2$. In a third case of disalicylaldehydo-titanium dichloride (dichelated metal), one molecule of the chelate was eliminated giving an apparently five-co-ordinated molecule of the formula $(C_7H_5O_2)Ti[(O_3(PO)_2(OR)_3]$ (R = ethyl, n-butyl).

From the reaction between $TiCl_4$ and dimethyl sulphate in 1:2 molar ratio, a new compound of the composition $ClTi(SO_4)CH_3SO_4$ was isolated as an insoluble yellow hygroscopic powder, soluble with decomposition in alcohols. The monochloride reacted with phenol, acetylacetone, salicylaldehyde and methyl salicylate to give substituted products of the type $(RO)Ti(SO_4)CH_3SO_4$ as coloured powders, insoluble in ordinary solvents and less hygroscopic than the parent monochloride. Identical compounds could be prepared by the action of dimethyl sulphate upon the corresponding organoxy-titanium trichlorides.

Bis-(methylsulphato) derivatives of organoxy-titanium compounds were prepared by the action of dimethyl sulphate upon the corresponding organoxy-titanium dichlorides. Thymol, vanillin, dibenzoyl methane and benzoyl acetone were the chelates used. Similarly, the *mono*- (methylsulphato) derivatives were prepared from triphenoxy- and trivanillino-titanium chloride. Oxy-titanium *bis*-(methylsulphate), $TiO(CH_3SO_4)_2$ was the product of reaction between dimethyl sulphate and diacetoxy (or dibenzoxy) - titanium dichloride. It is a white powder, soluble only in alcohols and decomposing above 110°.

O-Phenylenedioxy titanium dichloride $C_6H_4O_2TiCl_2$ was prepared as a brown powder from catechol (1 mol) and $TiCl_4$ (>2 mol). With excess of catechol the product was a red tricatechoxy derivative of titanium $C_6H_4O_2Ti,[OC_6H_4OH]_2$. Resorcinol, like catechol readily reacted with $TiCl_4$ and gave $C_6H_4O_2TiCl_2$, which, with excess of resorcinol gave a red monochloride, $C_6H_4O_2Ti(OC_6H_4OH)Cl$. These compounds were insoluble in benzene, light petroleum and chloroform but soluble in pyridine and alcohol.

New compounds such as thymoxy-titanium trichloride, tetrathymoxy-titanium, vanillino-titanium trichloride, divanillino-titanium dichloride and trivanillino-titanium chloride were prepared from the corresponding phenols and $TiCl_4$ under appropriate conditions. Phenoxyacetic acid with $TiCl_4$ gave two products, the orange-red diphenoxyacetoxy-titanium dichloride and yellow phenoxyacetoxy-titanium trichloride, both insoluble in common non-hydroxylic solvents.

Phenol, catechol and resorcinol each reacted with dichelated titanium dichlorides eliminating HCl and forming coloured chlorine-free solids. The chelates used were salicylaldehyde, methyl salicylate and dibenzoyl methane.

These yellow to chocolate-brown solids are not hygroscopic, stable up to 200° without melting, and insoluble or slightly soluble in benzene and other non-hydroxylic solvents.

8.2 *Diphenyl dithiophosphinic acid complexes with metals*

Relatively little is known on metal complexes in which the metal is bonded to sulphur atoms only, and on the resultant properties as compared with similar complexes bonded through oxygen or nitrogen. Some compounds of the title acid with polyvalent metals were prepared.

Compounds of diphenyl dithiophosphinic acid, PH_2PSSH, with copper (I), cobalt (II), nickel (II), and chromium (III) were reported earlier. These are of the general formula ML_X where X is the valency of the metal and LH is the ligand in which the PSS group appears to function as a bidentate chelate. Titanium tetrachloride reacts with the ligand in benzene to form the benzene adduct $Cl_2Ti(S_2PPh_2)_2 \cdot 2C_6H_6$, a red crystalline product which could be desolvated by heating in vacuum. Similar solvated compounds were obtained with stannic chloride in benzene and of the cobalt (II) compound with pyridine. Compounds of silver (I), zinc (II), cadmium (II), mercury (II), thorium (IV), chromium (III), uranyl (II) and manganese (II) were prepared by reaction of suitable salts of the metals with the ligand in ethanol and studied. The black iron compound appears to be a ferrous complex of the composition $2\,Fe(S_2PPh_2)_2 \cdot (Ph_2PS_2)_2$, the adduct disulphide resulting from mild oxidation of ligand by the ferric chloride used in the preparation.

8.3 *Coordination compounds, their semi-aromaticity and isomerism*

A study of the quasi-aromaticity of metal chelates, which may lead to new synthetic routes and novel reactions has been undertaken. In further proof of the quasi-aromatic nature of metal chelates (which has been brought out by our earlier work through several nitration reactions), many of the metal chelates have been thiocyanated and brominated[28].

8.3.1 *Thiocyanation studies* : Using thiocyanogen, Be (II), Al (III) and Mn (III) acetylacetonates have been thiocyanated. Whereas Be and Al chelates yielded the γ-thiocyanato-acetylacetonates, from Mn (III) acetylacetonate, only the thiocyanated ligand was obtained[40].

8.3.2 *Bromination* : Bromine which is supposed to bring about destructive bromination of metal chelates has been successfully used in conjunction with powdered calcium carbonate for the bromination of metal chelates. The studies revealed that the destruction of chelates occurring in presence of bromine and reported by earlier workers, is due mainly to the reducing properties of hydrogen bromide liberated in the course of bromination. Thus, though calcium carbonate was effective in warding off the adverse effects of hydrogen bromide in the case of aluminium, beryllium and chromium acetylacetonates, it was ineffective in the case of copper (II) and cobalt (III) acetylacetonates. The failure to obtain the desired products in the case of Cu (II) and Co (III) chelates is attributed to the facility of reduction of these metals.

8.3.3 *Monochloro and dichloro acetoacetanilide complexes of titanium* (IV) : A dichlorotitanium compound similar to dichloro-*bis*-(2,4-pentanediono) titanium (IV) whose structure has been much discussed in recent years was isolated by reacting titanium tetrachloride with acetoacetanilide. Of special interest is the isolation of monochloro-*tris*-(4-anilido-2,4-butanediono) titanium (IV) since this raises the important question of the co-ordination number of titanium. Reflectance spectra and X-ray powder data of these two new compounds have also been recorded.

8.3.4 *Isomerism of tris*-(acetoacetanilido) chromium (III) : *Tris* (acetoacetanilido) chromium (III), an inert octahedral chelate was isolated and resolved into two possible geometrical isomers, a deep green *cis*-isomer, m. p. 204° and a light-green *trans*-isomer, m. p. 226-27°. The infrared spectra of these compounds have been recorded. Thermograms of these isomers both in air and in nitrogen are also recorded. It appears that there is a small but significant difference between these two isomers, the *trans*-compound being thermally more stable than the corresponding *cis*-compound.

8.3.5 *Colour isomerism of bis-(salicylaldoximato) copper (II)*[38] : Although the colour isomers of some copper chelates are known, this work has proved the existence of colour isomers of *bis*-(salicylaldoximato) copper (II) for the first time. Several colour isomers of the compound have been prepared and studied. The compounds show distinct differences especially in the shades of colour and decomposition temperatures. Reflectance and infrared spectra have been recorded to characterize such compounds as individual entities. X-ray crystallographic studies have been made and the results clearly establish the existence of at least two forms of *bis*-(salicylaldoximato) copper (II). The other isomers show minor differences only, presumably due to the fact that during the process of crystallization, the molecules are packed in a slightly different way. Assuming that the crystal field effect is not limited to the near neighbour interactions only, the splitting of the electronic levels t_{2g} and e_g may be somewhat different from compound to compound leading to this difference in colour or shades of colour.

8.4 *Coordination polymers*

Preparative techniques of inorganic coordination polymers and their properties are being studied. Earlier studies on *bis*-(8-hydroxy-5-quinolyl) methane and titanium have been extended to two other quadrivalent elements viz. Sn and Zr.

Most of the work on coordination polymers reported in the literature is concerned with di-and tri-valent metals only. Synthesis of coordination polymers of *bis*- (8-hydroxy-5-quinolyl) methane with quadri-valent elements like Ti (IV), Sn (IV) and Zr (IV) have been achieved for the first time. The thermal stability of these polymers has been examined. It is apparent that the increasing atomic number of the metal results in enhanced thermal stability.

Work on another interesting *bis*-ligand, resorcinol 2:4-dialdehyde was also carried out. Coordination polymers of Cu (II), Ni (II), Co (II) and Zr (II) with this chelate ligand having potential polyfunctional coordination sites are synthesised. The NMR 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 757·5 cps and 761 cps represent protons of the two phenolic functions and the signals at 587 cps and 628 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 structure of these coordination polymers could be easily visualized.

8.5 *Infrared studies of coordination compounds*

Work has been undertaken to find out the metal-ligand stretching vibrations, as well as to trace any difference in compounds having different geometrical configurations and also to examine the effect of coordination or the perturbing crystalline field on the symmetry of groups inside and outside the coordination sphere.

The following compounds have been studied by nujol mull spectra :

(1) cis- $[Co(NH_3)_4Cl_2]Cl$;
(2) trans-$[Co(NH_3)_4Cl_2]HSO_4$;
(3) cis-$Na[Co(NH_3)_4(SO_3)_2]$;
(4) trans-$Na[Co(NH_3)_4(SO_3)_2]2H_2O$;
(5) cis-$NH_4[Co(NH_3)_4(SO_3)_2].3H_2O$;
(6) cis-$[Co(NH_3)_4H_2OCl]SO_4$;
(7) $Na_5[Co(CN)_4(SO_3)_2].12H_2O$;
(8) cis- $[Co(NH_3)_4CO_3]NO_3$;
(9) cis-$[Co(NH_3)_4C_2O_4]Cl$;
(10) $[Co(NH_3)_3H_2OCl_2]Cl$;
(11) and (12) $[Cr(NH_3)_3H_2OCl_2]Cl$

Although from these spectra it was possible to locate the metal-nitrogen stretching modes, metal-chlorine stretching modes, N-M-N bending modes etc., it was found that the spectra in general are more complex than expected.

Trans- [Co $(NH_3)_4Cl_2]^+$ should show one Co-N stretching mode, while the cis-[Co $(NH_3)_4Cl_2]^+$ should show four Co-N stretching modes. At least three such Co-N stretching vibrations were located for the *cis*- [Co $(NH_3)_4$ $Cl_2]$ Cl. However the case of *cis* and *trans* isomers of the sulphito complexes are found to be rather complex.

The solvent-cum-deuteration infrared spectral studies of salicylaldoxime and related compound confirmed the presence of intermolecular and intramolecular hydrogen bonding. The salient features of the infrared spectra of salicylaldoxime and those of its chelates with bivalent metals like nickel (II), copper (II), cobalt (II), manganese (II) and palladium (II), have been brought out by comparing their spectra with those of deuterated salicylaldoxime and deuterated nickel (II) chelate.

8.6 *Phosphors*

Phosphors are finding growing importance in the field of glowing paints etc. Study has been undertaken to synthesize zinc sulphide type and alkaline earth halophosphate type phosphors.

Several elements including the rare earths in varying compositions were studied as activators and sensitizers for synthesizing different calcium halophosphate phosphors.

With a view to finding the effect on luminescence intensity, studies were carried out by doping the calcium halophosphate phosphors with other compounds such as those of zinc, cadmium and beryllium. Improved fluorescence was noticed in all these cases. An instrument for measuring fluorescence was set up and spectral energy distribution measurements of the plain as well as the doped calcium halophosphate phosphors were carried out by irradiating small plaques oft hese phosphors by UV (2537A°) radiations. Crystallographic data on some of these synthetic phosphors are being collected by using X-ray powder pattern technique.

8.7 *Chromatographic adsorbents*

Conditions for the preparation of chromatographic grades of calcium hydrogen phosphate, calcium oxide, magnesium trisilicate, magnesium oxide, magnesium carbonate and bone meal have been standardised.

8.8 *Fluorine chemicals*

The fluorspar deposits of Gujarat, Rajasthan and Madhya Pradesh can be expected to form the basis of a sizeable fluoro-chemicals industry in India. High grade fluorspar finds its prime use in the production of hydrogen fluoride which is needed for the production of various fluorochemicals such as freon type used as refrigerants, fire retardants, aerosol propellants, fluorocarbon resins, plastics , lubricants etc.

Basic research on the preparation of various fluorine chemicals is being carried out.

In the study of different fluorinating agents for the preparation of organic and inorganic fluorides, it was observed that potassium hexafluoroantimonate, $KSbF_6$ is a convenient laboratory reagent for replacing moderately reactive chlorine atoms. Sodium silicofluoride also showed some activity in this direction. Arsenic trifluoride was found to be very active fluorinating agent (F for Cl) but it is very toxic and volatile.

Chloral condensation products of acetyl acetone, dibenzoylmethane and a compound believed to be the di-o-acetate of 1, 1-dibromo, 2, 2-dihydroxyethane have been prepared. The structures of these are being worked out with a view to prepare analogous fluorine-containing model compounds.

In dry nitrogen at 460° potassium hexafluoromanganate is found to decompose to a compound of approximate composition – $K_2Mn\ F_4$

Several attempts have been made to prepare ammonium hexafluoromanganate of tetravalent manganese from ammonium permanganate, hydrofluoric acid a reducing agent. So far, a complex of only trivalent manganese has been isolated.

Starting from benzidine and fluosilicic acid, optimum conditions for the preparation of silicofluoride of tetrazotised benzidine have been worked out. An overall yield of 80% has been obtained. The diazonium salt of α – amino anthraquinone has also been prepared by a similar method.

A reaction of aluminium fluoride and sodium fluoborate solution was studied and a conversion of aluminium fluoride to cryolite was obtained in good yields.

P. 9 PHYSICO ANALYTICAL CHEMISTRY

Standardization of raw materials, intermediates and finished products often demands developmental work in testing and chemical examination. Besides, it also involves study of new reactions which may lead to new analytical procedures for specific situations. Such a physico-analytical aspect involves modern techniques such as ultra violet, visible spectrophotometry, emmission spectroscopy, flame photometry, polarography, ion exchange etc.

9.1 *Analytical service*

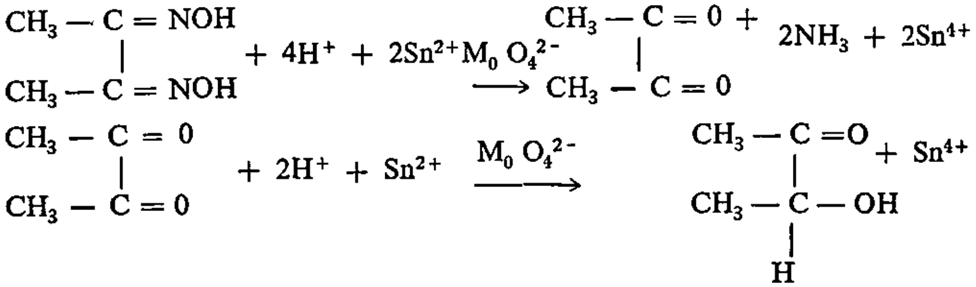
A veriety of materials concerning the various projects in the laboratory have been analysed for major constituents and/or trace impurities. The representative samples include 8-hydroxyquinoline, diphenylcarbazide, orthophenanthrolene, spent vanadium pentoxide catalyst, colour standards for butyl phthalate, aluminium-zinc alloy, chromium in ilmenite, mercury chloride, aluminium chloride, sodium cyanide, rubber seals, sulphides of cadmium, lead and zinc, and oxides of zinc, nickel and manganese.

9.2 *New methods of analysis*

Based on colour reactions of diacetyl monoxime with rhenium and molybdenum in the lower oxidation states, sensitive procedures for the two elements have been developed. The molar extinction coefficient for rhenium and molybdenum are 19,000 at 500 m μ and 8000 at 490 m μ respectively. This method for rhenium is very selective; even molybdenum does not seriously interfere.

9.3 *Mechanism of the molybdate dimethyl glyoxime reaction*

Stannous chloride in presence of molybdate quantitatively reduces dimethyl glyoxime (and / or diacetyl monoxime) in 3N HCl to ammonia and acetoin. The reduction of acetoin proceeds through diacetyl. Solutions of dimethyl glyoxime in dilute hydrochloric acid undergo hydrolysis to give diacetyl monoxime and hydroxyl amine. A decrease in acid concentration decreases both the rate of hydrolysis and the rate of catalysed reduction. These reactions are slowed down by alcohol or acetone. The immediate production of a deep violet colour on mixing a mixture of molybdate and dimethyl glyoxime with stannous chloride is caused by the formation of an unstable complex between tetrapositive molybdenum and diacetyl monoxime. At acid concentrations lower than 0.5 N HCl the colour obtained is a reddish violet due to complex formation between dimethyl glyoxime and tetrapositive molybdenum.



$$\begin{array}{l} CH_3 - C = NOH \\ \qquad | \\ CH_3 - C = NOH \end{array} + 4H^+ + 2Sn^{2+} M_0\, O_4^{2-} \longrightarrow \begin{array}{l} CH_3 - C = 0 \\ \qquad | \\ CH_3 - C = 0 \end{array} + 2NH_3 + 2Sn^{4+}$$

$$\begin{array}{l} CH_3 - C = 0 \\ \qquad | \\ CH_3 - C = 0 \end{array} + 2H^+ + Sn^{2+} \xrightarrow{M_0\, O_4^{2-}} \begin{array}{l} CH_3 - C = O \\ \qquad | \\ CH_3 - C - OH \\ \qquad | \\ \qquad H \end{array} + Sn^{4+}$$

9.4 *Direct reduction of insoluble vat dyes in the solid state at the dropping mercury electrode*

In contradistinction to the polarographic oxidation of the vats from solution, some insoluble vat dyes suspended in aqueous sodium hydroxide have been found to undergo electroreduction at the d. m. e. to give rise to maxima-shaped peaks. The peak potentials are characterisitic for a given vat dye being reproducible, while the peak currents depend on several parameters such as the particle size, rate of stirring etc., but are as a rule, much higher than the anodic diffusion currents obtained from the respective vats.

Accordingly, following dyes have been examined : indanthren yellow FFRK (CI 69,000); 1-1' dianthrimide; indanthren Brown Br (CI 70,800); indanthren yellow 3R (CI 70,805); indanthren Khaki GG (CI 71,050) and indanthrone (CI 69,800).

The thermodynamic significance of the peak potentials, which is not clear is under investigation.

P-10 NATURAL ORGANIC PRODUCTS

10.1 *Oleoresins and resinoids*

Work on these indigenous forest products was initiated with a view to study their chemistry for assessing their commercial utility. The oleoresins from *Dipterocarpus pilosus* (Hindi–Deodar) and *Hardwickia pinnata* (Mal.-Shurali) have been completely studied.

10.1.1 *Ailanthus malabarica* (Mal.– Mattipal) : The resin has been found to be a complex mixture of triterpenes possibly of the dammarane group. Eight new compounds have been isolated and work on their structure elucidation is an progress.

10.1.2 *Boswellia serrata* (Hindi - Salai) : The material is procured from Madhya Pradesh. The gum has been separated into acidic and neutral components. Acidic components have been examined in detail and have been found to consist of β -boswellic acid; its acetate and the 11-oxo–derivative and a few other minor components are being characterised.

10.2 *Wood extractives*

This work was initiated to study the chemistry of extractives from commercially important timbers of India.

Cedrela toona (Hindi - Tun) : From the non-volatile portion, a new degraded triterpene, similar to cederelone has been isolated. Its structure determination is in progress.

10.3 *Hamycin*

Hamycin, an antifungal antibiotic of clinical value discovered by Hindustan Antibiotics Ltd. Pimpri, is produced by a streptomyces strain from the soil of Pimpri. Besides the fact that hamycin belongs to the class of heptaene antibiotics, little is known about its chemistry.

Hamycin as obtained from the Hindustan Antibiotics could be separated into three fractions by partitioning with solvents. The biological active fraction from preliminary data obtained so far appears to be either identical or very similar to trichomycin.

10.4 *Carbohydrates*

10.4·1 *Modification of indigenous gums for use as substitutes for gum arabic :* At the instance of Indian Posts and Telegraphs Board, easily available indigenous gums are being modified for use as substitutes for gum arabic. Presently, Post & Telegraphs Department use imported gum arabic for general adhesive purpose and for use on teleprinter papers.

Indigenous gums such as ghatti, jeol, karaya, babul and cashew have been examined. Two new methods for modifications have been developed. Small samples of some of the modified gums have been approved by P & T Board. On their request, larger samples have been prepared and supplied for trials in different parts of the country.

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

10.4.2 *Studies in indigenous gums* : Chemical structure of the gum from *Terminalia tomentosa* (Marathi–Ain) is being investigated with a view to suggest its proper utilisation.

The gum has been found to consist mainly of D–galactose, D–xylose and L–arabinose. The minor components are L–ramnose and D–glucuronic acid. Four chromatographically pure oligosaccharides have been obtained by partial degradation of the gum and structures of two of them have been established as

(i) 3-O-β-D-galactopyranosyl-D-galactose m. p. 157-58°, $\alpha]^{32}_{D} +$ 64.0°, and (ii) 3-O-β-D-galactopyranosyl-D-arabinose m. p.199-202° $\alpha]^{30}_{D} +$ 63.3°.

10.5 *Utilisation of groundnut shells*

Earlier work in this laboratory showed that groundnut shell lignin is quite different from the normal tropical wood lignin and gives mainly vanillin, uncontaminated with syringic aldehyde, on oxidative cleavage. Various oxidizing agents were employed and pure vanillin was obtained in different yields.

Groundnut shell have also been sent to a paper factory for pulping by the sulphite process. The lignosulphonic acid obtainable from the sulphite liquor will be processed for the production of vanillin.

Groundnut shell pulp obtained by different methods are being saccharified for the production of glucose. During the course of this work a simple spot test for the determination of vanillin and some other carbonyl compounds was developed[49].

10.6 *Medicinal plants*

10.6.1 *Berberis aristata* (Hindi – Chitra) : After the sucessful completion of the sponsored project on isolation of berberine hydrochloride from berberis bark, studies in the pharmacological activities pertaining to the reported medicinal properties of berberine have been undertaken in collaboration with the authorities of Grant Medical College, Bombay.

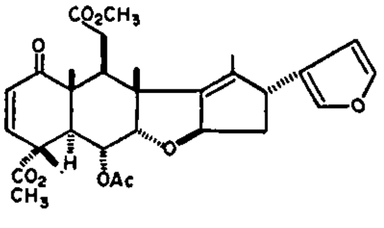
10.6.2 *Ougeinia dalbergioides, Benth* (Hindi – Sandan) : Various medicinal properties have been reported for the different parts of this plant. The stem bark is stated to be toxic to catterpillar pests and fish. The exudation of the bark is useful in diarrhoea, dyscentery etc.

The chemical investigations of the bark have revealed the presence of two pentacyclic triterpene alcohols identified as lupeol and betulin and a saponin, which on hydrolysis furnishes another triterpene characterised as β–amyrin[57].

10.6.3 *Balanophora indica* : This plant is a root parasite and causes destruction in coffee plantations. Tubers of the plant are being investigated for the chemical constituents and for suggesting possible remedies against these infections.

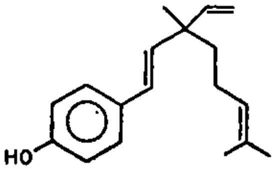
Chemical investigations on stems of Ruta graveolens, leaves of *Viola odorata* (Hindi – Banafsha) and whole plant of *Astercantha longifolia* (Hindi-Talimakhana) have also been undertaken.

10.6.4 *Malia azadirachata Linn* (Hindi–Neem) : Neem is one of the common trees found all over India and preparations from different parts of the tree are being used in ayurvedic medicine for various ailments.The chemistry of the main crystalline bitter constituent, nimbin, obtained mainly from the bark and the oil, was thoroughly investigated. From the chemical and physical data the structure, stereochemistry and absolute configuration have been ascertained[61,64].



Studies on the pharmacological activity of the derivatives of nimbin and other neem products have been undertaken.

10.6.5 *Posoralea corylifolia Linn* (Bakuchi) : Hexane extract of whole fresh mature seeds of the plant has been found to contain as the major component, a novel mono-terpenoid phenol which has been named Bakuchiol after its Sanskrit name. Its structure has been determined on the basis of systematic degradative studies.



10.7 *Essential oils*

A number of Indian plants are known for their medicinal properties and use in perfumery. However, a critical examination of the essential oils obtained from these, with the help of modern techniques, has not been done so far. With a view to isolate and characterise the various constituents, a systematic examination of the oils from the following plants was undertaken.

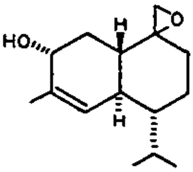
10.7.1 *Vetiveria zizanioides.* Vetiver, (Hindi-khus) : The tricyclic sesquiterpene primary alcohol $C_{15}H_{24}O$, containing one exo-methylene double bond, was shown to have a new carbon skeleton, the CH_2OH being attached to a cyclopentane ring, fused to two other rings. Work on the structure elucidation of other primary and secondary alcohols of the oil is in progress.

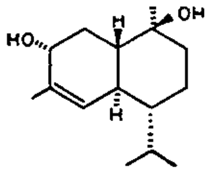
A new leavo-rotatory alcohol khusinoloxide, $C_{15} H_{24} O_2$ isolated from North Indian vetiver oil is shown to possess the structure and stereochemistry as presented by (I). It also belongs to the antipodal group of compounds.

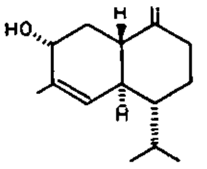
On the basis of both chemical and spectral evidences, khusinodiol, the main product of the BF_3 reaction of khusinol (III), has been assigned the stereostructure (II). The hydrocarbon from the same reaction is shown to be (IV). The dienemonol (V), (+) ∝-cadinol (VI) and iso-khusinol (VII) have been prepared from khusinol.

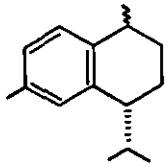
Further examination of the alcohol fraction of North Indian vetiver oil has lead to the isolation of four more alcohols. They include (1) khusimol (same as the tricylic primary alcohol isolated from South Indian veriety), (2) (—) – δ – cadinol (VIII), and (3) two unidentified alchohols designated as A and C. Besides these alcohols, (—) γ–cadinene (IX), a hitherto unreported antipodal hydrocarbon has also been isolated from the hydrocarbon fraction of the oil.

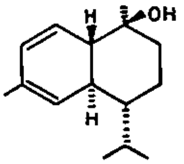
The acid fraction of the oil was found to consist of a mixture of six acids by GLC and TLC data. Of these, three of them namely, those derived from khusol, khusilal and khusinol (X and XI) have been identified as their methyl esters by GLC analysis, employing peak accentuation technique and by comparing the R-dye values on TLC. Work on khusimol, alcohols A & C is in progress.

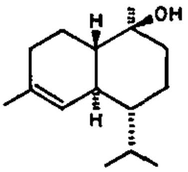

I

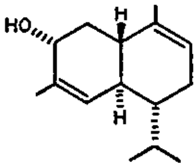

II

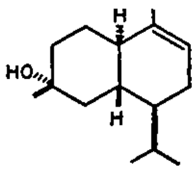

III

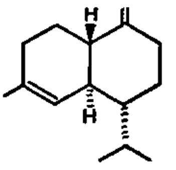

IV

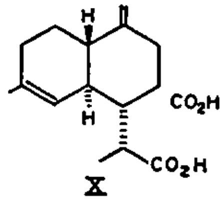

V

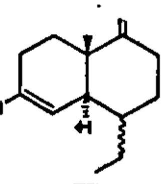

VI


VII


VIII


IX


X



XI

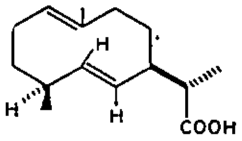
10.7.2 *Sassuria lappa clarke*. Costus root, (Kashmir variety) (Hindikuth) In addition to the formation of santanolide ' c ' (II) from the acid (I) during its acid catalysed cyclisation, a monoethenoid bicyclic acid (III) could also be obtained from the reaction products, which is shown to possess the structure (III).

The absolute configuration of parthenolide (IV) at C_6, C_7 and the position of the tri-substituted double bond between C_{10} and C_1 were established, by preparing a diepoxide (V) from solid dihydrocostunolide (VI), which was identical in all respects with the monoepoxide (V) of dihydroparthenolide (VII).

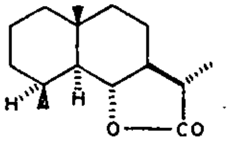
The structure of the ketocarboxylic acid (VIII) prepared from the alcohol (IX), obtainable from dehydrocostus lactone, has been established on the basis of the formation of a cross conjugated dienone carboxylic acid ester (X) by bromination and dehydrobromination.

The alcohol (XI) obtainable from (VI) containing a cyclo-deca- 1:6 diene system gave a monoethenoid bicyclic alcohol (XII) of the guaine type on thermal rearrangement. The stereochemistry of 12-methoxydihydrocostunolide (XIII) at the position C_{11} has been determined by an un-ambiguous chemical method, which shows that the methoxymethylene group at C_{11} is β–oriented and not α–as presumed on the basis of the comparison of rotation contributions with solid dihydrocostunolide (VI).

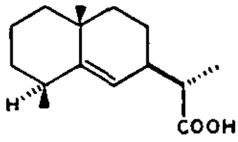
The petroleum ether exhausted costus root powder has been extracted with different solvents by percolation and the extracts are being examined. Inulin has been isolated from the aqueous extract of the powder.



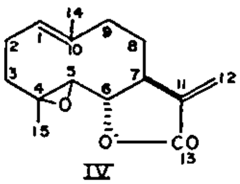
I



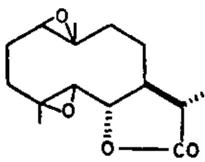
II



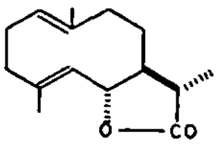
III



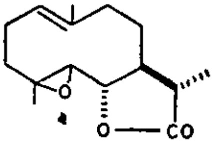
IV



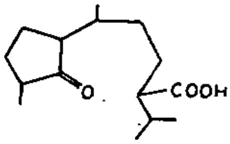
V



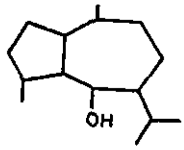
VI



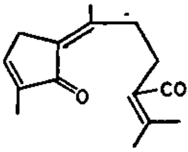
VII



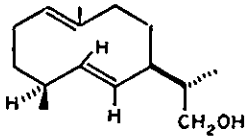
VIII



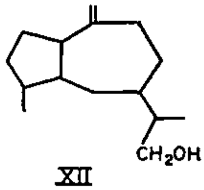
IX



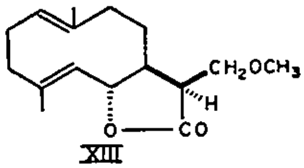
X



XI



XII



XIII

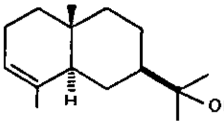
10.7.3 *Valeriana wallichi.* Valerian root, (Hindi-Tagar) : The valerian root oil (concrete) from adjoining areas in the Himalayan regions has been subjected to steam distillation and the distillate separated into acidic and neutral parts. The acidic portion contains isovaleric and caproic acids. The neutral portion contains calarene, β–bergamotene, α–curcumene and valeranone.

10.7.4 *Nardostachys jatamansi* DC. (Jatamansi) : In addition to the compounds reported earlier, a new oxide, hydrocarbons, a polyoxygenated crystalline solid m. p. 77-78° together with α–eudesmol (I), β-eudesmol (II), elemol (III) angelicin (IV), 4-hydroxy thymol dimethyl ether (V) have been isolated and characterised from the greyish brown variety of *Nardostachys jatamansi.* Structural elucidation of the polyoxygenated crystalline solid $C_{20}H_{30}O_4$ is in progress.

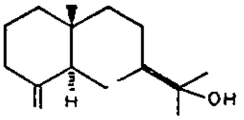
Other vasodilatory agents viz. (±) *cis*–visnadin (VI), suksdorfin (VII) and dihydropteryxin (VIII) have been prepared from Jatamansin in addition to the previously reported (±) *cis*-dihydrosamidin. Some interesting rearrangements have been observed during the preparation of (±) *cis*-suksdorfin and dihydropteryxin.

In continuation of the work on dark brown variety of *Nardostachys jatamansi* several hydrocarbons along with calarene (IX) aristolene (X), an α–β unsaturated aldehyde and two alcohols have been isolated.

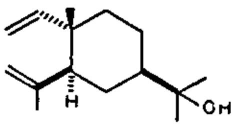
One of the alcohols, nardol has been assigned the structure (XI). The stereochemistry of nardol and structural determination of another alcohol $C_{15}H_{24}O$ are in progress.



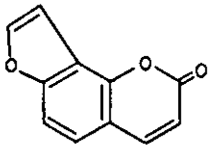
I



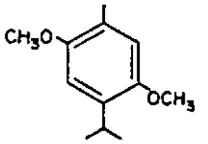
II



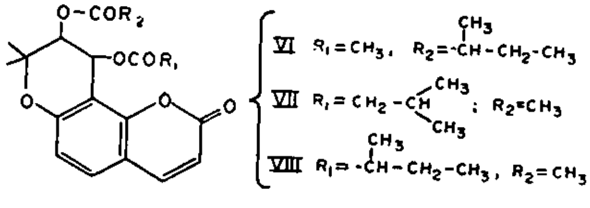
III



IV



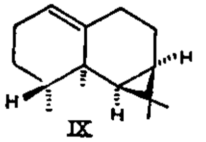
V



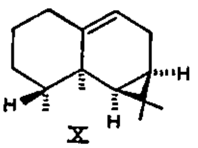
VI $R_1 = CH_3,\ R_2 = -\underset{}{\overset{CH_3}{\overset{|}{C}}}H-CH_2-CH_3$

VII $R_1 = CH_2-CH\genfrac{}{}{0pt}{}{CH_3}{CH_3}\ ;\ R_2 = CH_3$

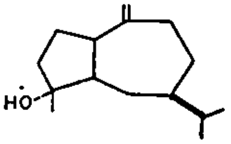
VIII $R_1 = -\overset{CH_3}{\overset{|}{C}}H-CH_2-CH_3,\ R_2 = CH_3$



IX



X



XI

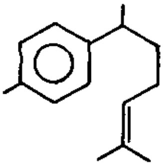
10.7.5 *Curcuma Longa.* Turmeric, (Hindi-Haldi) : Many of the plants beloging to the zingiberaceae family are widely used as spices and hence a systematic study of the essential oils derived from them has been undertaken. The chemistry of turmeric oil has been investigated.

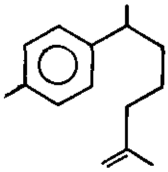
A convenient method for the preparation of (+) ar-turmerone from turmerone has been developed. Absolute configuration of (+) ar-turmerone and (+) ∝–curcumene has been established.

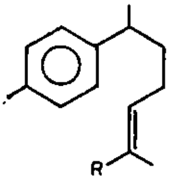
(±) ∝–Curcumene (I) free from the isopropenyl isomer (II) has been synthesised by two different routes. The acid (III) related to nuciferol (IV) has been synthesised.

The hydrazine reduction of the epoxide (V) derived from (+) ar-turmerone has been studied.

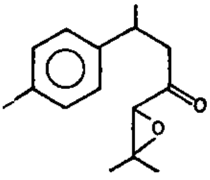
It is proposed to examine the other constituents of turmeric oil. The examination of ginger oil will also be undertaken.


I


II



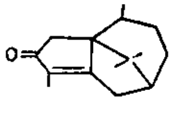
III R = -CO$_2$H
IV R = -CHO



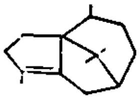
V

10.7.6 *Cyperus scariosus.* (Mar.–Nagarmutha) : 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 tubors of *Cyperus scariosus.*

On the basis of spectral and chemical evidences structure (I) has been assigned to isopatchoulenone. Iso-patchoulenone has been prepared from cyperene (II) by oxidation with tertiary butyl chromate. Further work regarding the stereochemistry of the ketone is in progress. Some new



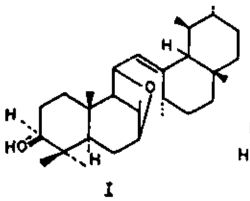
I


II

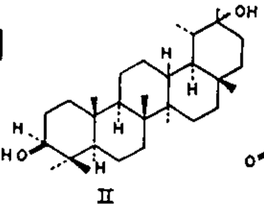
hydrocarbons and alcohols have been isolated from the same oil and the work on structural elucidation of these, is in progress.

10·7·7 *Inula recemosa* (Kashmir–Poshkar): Roots of *Inula racemosa* (from Jammu) are extracted with petroleum ether in the usual way to get an oil in 6% yield. After cooling the oil as such, at—20° some solid material separated out, which has been shown to consist of (1) alanta-lactone, (2) *iso*-alantalactone and dihydroalantalactone. Some interesting transformations of these have been carried out.

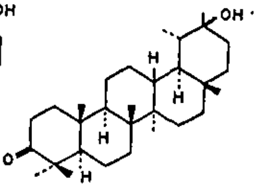
10·7·8 *Canarium strictum.* black dammer resin, (Mar.-Dhup) In addition to the compounds reported earlier three new triterpenes, oxidodammarol (I) epia-ψ-taraxastane diol (II) and the keto monol (III) have been isolated and their structures established on the basis of chemical and spectral evidences.



I



II



III

10·7·9 *Artemesia vulgaris L* (Hindi-Nagdona) : The petroleum ether extract of the plant *Artemesia Vulgaris L* has been examined and the presence of a large number of known compounds has been established. A new crystalline pentacyclic triterpene alcohol has been isolated and shown to be fern-9(11) ene-3-β-01.

10.8 *Plant pigments*

10·8·1 2, 2-*Dimethylchromenes :* A general method has been developed for the synthesis of 2, 2-dimethylchromenes, of which there are many representatives in nature. Evodionol methyl ether (6-acetyl-5, 7-dimethoxy-2, 2-dimethylchromene) and alloevodionol methyl ether (8-acetyl-5,7-dimethoxy-2, 2-dimethylchromene) have been synthesised. Work on the sythesis of munetone is in progress.

10.8.2 *NMR studies of phenolic ketones* : 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-hydroxyflavanones.

10·8·3 *Flavones from iretol* : The synthesis of 2, 4, 6-trihydroxy-5-methoxyacetophenone and 2, 4, 6-trihydroxy-ω-5-dimethoxyacetophenone by the Hoesch reaction was mentioned earlier. Using the former, hispidulin (dinatin) has been synthesised and the sythesis of several other naturally occurring flavones is in progress.

10·8·4 *Pigments of Garcinia species* : 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.

A new pigment has been isolated from the fruits of *Garcinia xanthochymus*. It has the molecular formula $C_{38}H_{50}O_6$ and its structure, mainly based on spectral data and our knowledge of the chemistry of morellin and the morellic acids, is under investigation.

10·8·5 *Hydroxyanthraquinones* : 1, 3, 6-Trihydroxyanthraquinone has been synthesised, 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 synthesised.

The structure of a second pigment accompanying cassiamin in *Cassia siamea* is under examination.

P.11 SYNTHETIC ORGANIC CHEMISTRY

11·1 *Studies in synthetic dyes*

11·1·1 *Azoic dyes* : Preliminary results on the application of NMR spectra to the study of azophenol-quinone hydrazone tautomerism, which is of general interest in connection with the structures of azo and azoic dyes were outlined in a recent paper *Chimia*, **19**, 213 (1965). More extensive data have now been obtained. It has been shown that the consideration of the deshieding effect of the azo group on the *ortho* and/or *peri*-protons of arylazo systems is adequate for the identification of the two forms; further evidence is provided by the lack of aromatic character in one of the rings of the hydrazone form, resulting in diamagnetic shifts of some of the protons.

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.

11·1·2 *Reactive dyes* : By condensing cyanuric chloride with 1, 2 or 3 molecules of hydrazine and interaction of the products with ethyl acetoacetate or ethyl benzoylacetate, dye intermediates containing 1, 2 or 3 pyrazolone units attached to *s*-triazine have been prepared and the preparation of azo and azoic dyes derived from them is being studied. Azo dyes derived from pyrazolone are mainly acid colours characterised 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, triazalotriazines have been prepared and their preparation and reactions are under study.

A systematic study of reactive dyes based on cyanuric chloride is being carried out with the main object of producing dyes with high bleach fastness. Incidentally, new types of such dyes are being explored.

The technical preparation of a reactive dye containing cyanuric chloride (Procion Red 5 BS) is in progress. Based on this experience, the preparation of a few other reactive dyes will be carried out. Experiments are also in progress to prepare a reactive dye containing copper phthalocyanine.

11.1.3 *Anthraquinonoid dyes* : 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-arylanthraquinones 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 this 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.

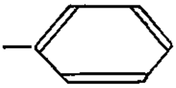
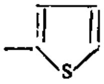
Work on the reductive methylation and acetylation of anthraquinonoid vat dyes, especially derivatives of violanthrone and isoviolanthrone, has been continued. A procedure for the thin-layer chromatography of solubilized vat colours has been developed and is being used for the isolation of the parent vat dyes in pure form. Work on steric effects in the light absorption of violanthrone derivatives has been continued.

11.1.4 *Sulphur heterocyclics and cyanic dyes :* The present work is an extension of the synthesis of polycyclic thiophenes and thiopyrans which was being carried out at the Department of Chemical Technology, University of Bombay.

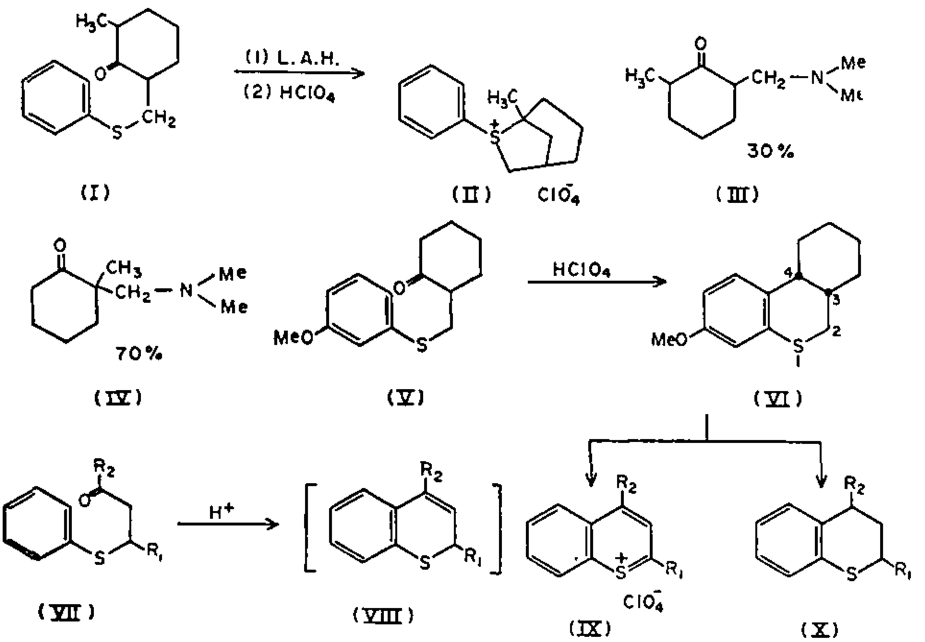
The cyclodehydration of β-aryl mercapto ethyl methyl ketones with polyphosphoric acid yielded a mixture of thiachromens and thianaphthalenium salts (which subsequently change in suitable cases, to thiacyanine dyes). A mechanism involving an acid catalysed intermolecular hydride shift from Δ^3-thiachromene has been proposed. The arylmercaptomethyl methyl ketones themselves, are readily prepared in good yields (72-99 %) by the base catalysed addition of aryl mercaptans to methyl vinyl ketones or by the interaction of aryl mercaptans with mannich bases derived from ketones.

Contrary to expectations, the condensation of thiophenol with mannich base from 2-methylcyclohexanone gave a poor yield (less than 20 %) of the ketosulfide [*J. Org. Chem.* 29, 1339 (1964)]. The reason for the low yield was later on traced to the presence of two isomeric compounds in the mannich base, (I) the fraction (III) leading to the desired condensation product (I). The reduction of (I) with lithium aluminum hydride gave the alcohol which on treatment with perchloric acid yielded (II). Further work on the confirmation of the structure proposed is in progress.

The studies on the stereochemistry of the hydride transfer at ring junction during the formation of thiachromans are in progress. The treatment of the ketosulfide (V) with perchloric acid gave the thiachroman (VI) which is considered to have been formed by the migration of a hydride form the 2-position of the Δ^3–thiachromene intermediate. Attempts are being made to find out whether the thiachroman (VI) so obtained has a *cis* or *trans* configuration at the ring junction (3/4) or is a mixture of the two. The catalytic hydrogenation of Δ^3–thiachromene would provide an authentic *cis* compound which would be used as a model for comparison.

The acid induced hydride transfer in the disproportionation of 4-and 2, 4-diaryl substituted Δ^3–thiachromene (VIII) was studied. The latter compounds, which are formed as intermediates when aryl-(aryl-3-oxo) alkyl sulfides (VII) are treated with a mixture of perchloric acid and trityl chloride, yielded the corresponding thianaphthalenium salts (IX) and thiachromans. (X) The factors which influence the intermolcular hydride transfer when R_2 = H, $-CH_3$,  and  are being studied by using perchloric acid alone as the catalyst and therefore in the absence of an hydride abstractor.

The ketones (VII) when they carry a p-dimethylaminophenyl substituent in the R_1 position, yield thiacyamine dyes. When such thiacyamine dyes have a thiamyl group in the R_2 position, then further delocalisation of the charge occurs and the thienyl sulfur atom also participates in the conjugation. This was indicated by the pronounced bathochromic shift (30 to 50 m μ) in the electronic spectra of the compounds. The studies on the electronic spectra of a series of thiacyanine, thicarbocyanine, hemithiacyanine, azathiacyanine and diazamerocyanine dyes, starting from 4-methyl-2-phenylthianaphthalenium perchlorate and 4-methyl-2-phenyl-1-thiaphenanthrenium perchlorate are in progress.



11.1.5 *Mechanism of formation of oxazine and dioxazine dyes and pigments :* The mechanism of formation of an oxazine type of dye (Meldola's Blue) is under investigation. Meldola's Blue was prepared by the condensation of β-naphthol with an excess of p-nitrosodimethylaniline hydrochloride. The reaction may proceed by the transfer of a hydride from the leuco base to another molecule of p-nitrosodimethylaniline. The incorporation of trityl chloride as an hydride abstractor in an equimolar mixture of reactants in acetic acid gave the dye and triphenylmethane, showing evidence of hydride transfer. The preparation of leuco base in pure form in order to study its conversion to the dye by hydride abstracting reagents is in progress.

11.1.6 *Dioxazine dyes and pigments* : This group includes some outstanding commercial dyes and pigments which possess high light fastness. They are at present not produced in India.

The mechanism of formation of dioxazine pigments is being examined as part of study of their chemistry and technology. The di-imine obtained by the reaction of aniline with chloranil, on treatment with trityl perchlorate in boiling acetic acid did not cyclise to the dioxazine. However, on carrying out the reaction in boiling monochloroacetic acid and addition of trityl perchlorate the di-imine was instantaneously converted to the dioxazine pigment. If the reaction was to proceed by the loss of a hydride, then an equimolar amount of triphenylmethane would be formed in the reaction mixture. Evidence for the formation of triphenylmethane is being looked into. It is interesting to note that the reaction did not take place when trityl perchlorate was replaced by trityl chloride or when the reaction was carried out in the absence of such hydride abstracting reagents.

A parallel series of reactions were also observed when the di-imine was prepared from o-phenetidine instead of aniline. The di-imine from β-naphthylamine and chloranil could be very readily cyclised to the dioxazine pigment (80% yield) by even much milder conditions such as simply boiling in o-dichlorobenzene or nitrobenzene. The various factors which influence the formation of dioxazines and their mechanism of formation are under study.

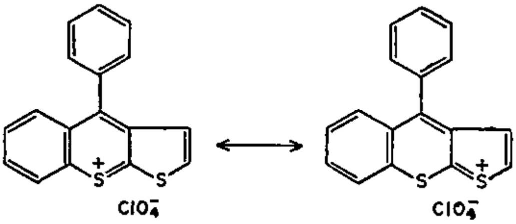
11.1.7 *Dyes for synthetic fibres :* The purpose of this investigation is to explore the possibility of making dyes for synthetic fibres with raw materials available in this country. The syntheses of newer and cheaper dyes for terylene and nylon and which have good affinity and fastness properties are also attempted employing simple anionic acid dyes as starting materials and converting them into water-insoluble dyes by suitable structural modifications. Several such dyes have been synthesised and their dyeing and fastness properties are being examined.

11.2 *Synthetic drugs*

11.2.1 *Carcinostatic compounds* : The synthesis of 10-N-methyl, 9, 10-dihydro-3,4-benzo-phenanthridine-9-mercapto acetic acid which would be of interest as a carcinostatic compound, is in progress. The condensation of 2-dimethylaminomethyl cyclohexanone with 2-naphthyl amine yielded 2-(β-naphthylamino)-methyl cyclohexanone which was cyclised with polyphosphoric acid to 3, 4-benzo-5, 6, 7, 8-tetrahydrophenanthridine.

11.2.2 *Bi-cyclic thiaxanthylium salts* : The synthesis of 9, 10-ethano-thiaxanthylium perchlorate is attempted with a view to study its biological activity. The treatment of thiaxanth-hydrol with perchloric acid gave the thiaxanthylium perchlorate which was condensed with diethyl malonate to yield the 9-diester. On hydrolysis and decarboxylation, the 9-acetic acid derivative was obtained. Lithium aluminium hydride reduction of the corresponding ethanol and the cyclisation stages are in progress.

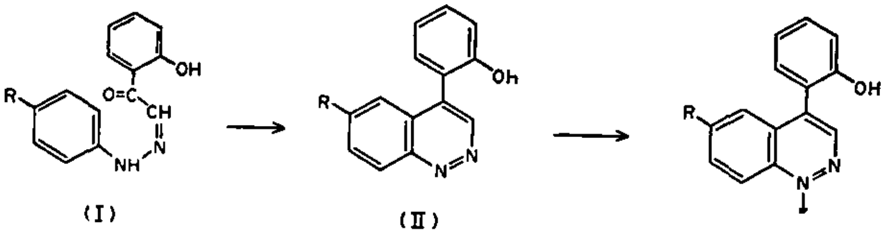
The syntheses of hitherto unreported cationic heterocyclic compounds containing sulfur where the charge can move from one hetero atom to another within the heterocyclic framework of the molecule is in progress. γ-Phenyl α, β-thienothiapyrelium perchlorate (XI) was prepared and its special comparisons (UV, IR & NMR) were made with that of 9-phenylthiaxanthylium perchlorate. The results indicate that the thiophene sulfur atom does not participate in the resonance. The α, β–thienothiapyrelium perchlorate as found to be unstable.



(XI)

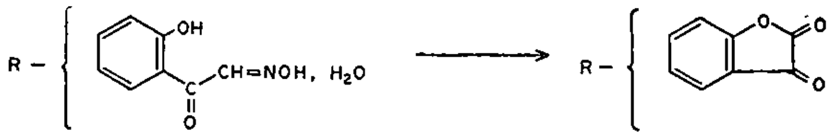
11.2.3 *4-(o-hydroxyphenyl)-cinnolines* : A new route has been found for the synthesis of hitherto unknown 4-(o-hydroxyphenyl)-cinnolines (II) of possible therapeutic value.

These cinnolines have been obtained by cyclization of o-hydroxyphenylglyoxal-2-phenylhydrazones. (I) with fused $AlCl_3^{62}$. where R = alkyl halogen of 4-(o-hydroxyphenyl)-cinnoline-1-N-oxide (III) has been prepared and will be sent for screening against cancer.



(I) (II)

11.2.4 *Meerwein arylation of 4-hydroxycoumarins* : During the course of arylation of 4-hydroxycoumarins by aryl diazonium chlorides (Meerwein's method) a side reaction was observed for the first time, which led to the preparation of hitherto unknown o-hydroxyphenylglyoxal-monoxime monohydrates (I) These have been found to cyclize easily to coumarandione derivatives (II)



(I)

11.2.5 *Apomorphine :* Various methops available in the literature for the production of apomorphine from morphine have been examined but have been found to be unsatisfactory.

11.2.6 *Conversion of thebaine to codeine* : The first step involving the conversion of thebaine into codenone has beeen investigated. A suitable TLC system for the analysis of thebaine and codenone mixture has been worked out.

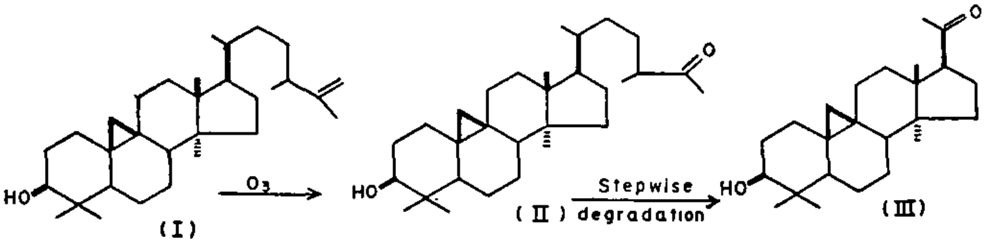
11.3 *Steroids*

11.3.1 *Regeneration of steroid alcohols from their methyl ethers :* In work on the chemistry of natural products, it is often necessary to protect aliphatic hydroxyl groups before attacking other sensitive centers of the molecule. Esterification of the hydroxyl group is not always useful, since, it may not give any protection even under mild alkaline conditions. Methylation does give the necessary protection under alkaline and mild acidic conditions, but there is no simple way to demethylate and regain the hydroxyl group from the methoxyl. The methods available at present either use too drastic conditions, which might break up sensitive parts of the molecule, or may not lead to the desired alcohol. A novel method has now been devised to achieve this end. A mixture of boron trifluoride etherate and acetic anhydride at 0° or below, has been found to cleave different types of steroidal methyl ethers.[54]

The mechanism of this type of cleavages has also been worked out. It involves the initial formation of an oxonium ion by the addition of BF_3 to the ether oxygen and cleavage of the carbon-oxygen bond from (a) the secondary carbon to give the elimination and epimeric products, and (b) from the methyl to give the product with retention of configuration by the nucleophilic attack of the acetate moiety of the acetic anhydride. The details of the mechanism has been confirmed by using different acid chlorides instead of acetic anhydride as the reagent and model compounds for the reaction.[56]

11.3.2 *Conformation of Westphalen's diacetate :* The conformation of a steroid rearrangement product known for over 50 years as Westphalen's Diol Diacetate has now been determined by NMR and IR spectroscopy of model compounds along with the diol diacetate. Its rings are found to exist as A/B *quasi-trans*, B/C *quasi-cis* and C/D *trans* with the C_6 β-substituent in the equatorial orientation.[58], [63]

11.3.3 *Modification of cyclolaudenol* : Step-wise degradation of cyclolaudenol (I) to the nor-compounds (II) has been standardized and its conversion into progesterone analogue step-wise is being studied. (III)

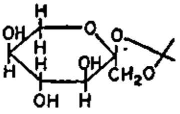


11.4 *Synthetic carbohydrates*

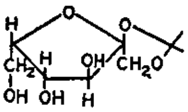
11·4.1 *Cellulose caprate :* Cellulose caprate with requisite degree of substitution is the main ingredient of an optical cement composition, imported at present. Conditions for the preparation of specified type of cellulose caprate were standardized. On procuring the two plasticizers required, the optical cement will be prepared and sent for trials.

11.4.2 *Cyclic acetals and ketals of monosaccharides* :

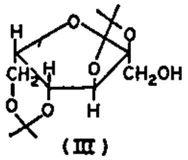
2, 3 : 4, 6-Di-o-isopropylidene-∝-L-sorbofuranose (DAS) which is produced by sulphuric acid catalysed acetonation of L-sorbose, is a key intermediate in the synthesis of vitamin C. Thin layer chromatographic studies of this acetonation reaction have revealed that DAS is formed through 1, 2-o-- isopropylidene-∝-L-sorbopyranose (I) (1-2-MAS).[66] This finding incidentally supports the mechanism independently proposed recently by Japanese workers. The acetonation reaction was further studied with different catalysts. In the case of copper sulphate catalysed acetonation of L-sorbose, it was found for the first time that in addition to 1, 2-MAS (I)



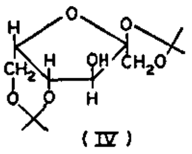
(I)



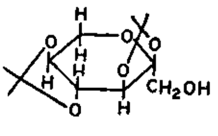
(II)



(III)



(IV)



(V)

a new MAS, the structure of which has been established as 1, 2-O-isopropylidene-α-L-sorbofuranose (II) and three di-O-isopropylidene derivatives of L-sorbose are also formed (III, IV and V) of which structures (IV and V) were estabished by us.

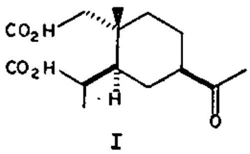
New interesting findings have been noted in these studies of acetalation and ketalation of various other monosaccharides on which detailed work has been undertaken.

11.4.3 *Preparation of carbohydrate derivatives required as fine chemicals*: Optimum conditions for the laboratory scale preparations of the following carbohydrate derivatives have been standardized and supplies have been made through FCP. D-glucosamine hydrochloride from crab and prawn shells, diethylaminoethyl cellulose and acetobromoglucose.

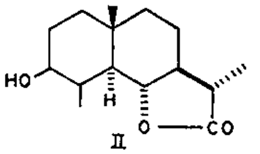
On demand from a research institute from USA, phenyl-β-D-galactoside has been prepared and part requirement has been exported.

11.5 *Transformations and synthesis in terpenoid series* :

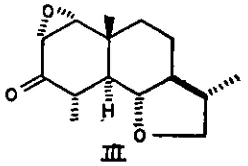
11.5.1 *Compounds related to selinane and elemane* : A large number of



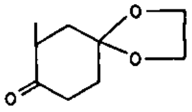
I



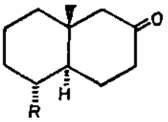
II



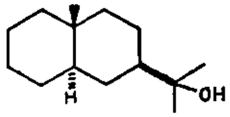
III



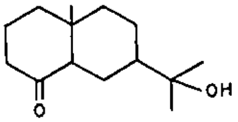
IV



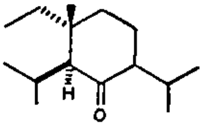
V. R=H
VI. R=CH$_3$



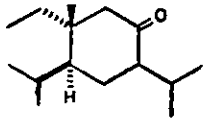
VII



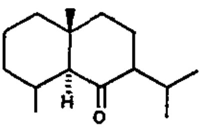
VIII



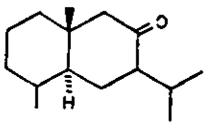
IX



X



XI



XII

selinanic compounds occur in nature and some of them such as santonin are of medicinal importance. A systematic study of the synthesis and reactions of these compounds has been undertaken. Junenol, isojunenol, dihydrojunenol tetrahydrosaussurea lactone, 4. epi-dihydroeudesmol and the ketocarboxylic acid (I) related to elemane have been synthesised.

The stereochemistry of a hydroxylactone(II) obtained in 70 % yield from the hydrogenation of santonin has been established. The elimination reactions of a number of esters of (II)have been studied. This has led to improved methods for the preparation of sant-2-enolide, sant-3-enolide and santanolide 'c' from santonin. A number of 1-oxo eudesmanes have been synthesised utilising the hydrazine reduction of α, β-epoxy ketone. (III).

Tetrahydro elemol, elemane 2, 3, 12 trioic acid and elemane 2, 3, 12 triol have been synthesised. Imporved methods for the preparation of ketoketal (IV), an important intermediate for triterpenoid synthesis have been developedl The decalones (V) and (VI) and the alcohol, (VII) have been synthesised. The Huang-Minlon reduction of the keto alcohol (VIII) has been studied. Tetrahydroelemol and dihydroeudesmol have been transformed into the ketones (IX, X, XI) and (XII) by a series of reactions. The ketone (X) has also been prepared from germacrone. Some interesting transformations of the alcohol obtained from (XII) have been carried out.

Dihydroeudesmol has also been converted into dihydrocostol, tetrahydrocostol and santanolide 'c' by an interesting series of reactions.

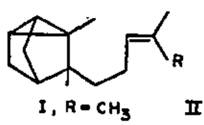
11.5.2 *Compounds related to guaiol* : Both solid and liquid dihydroguaiols have been converted into hexahydrodehydrocostus lactones by a series of reactions. The corresponding guainanes from the two alcohols have been prepared.

11.5.3 *Transformations in the longifolene series* :

Longifolic acid obtained during the oxidation of longifolene has been converted into a series of compounds including half esters and their degradation products. Critical examination of the products is in progress. Some interesting transformations of *iso*-longifolic acid have also been carried out.

11.5.4 *Transformation products of tricycloekasantalic acid* :

By application of Wittigs reaction at some of the stages, tricycloekasan-



I, $R = CH_3$ II, $R = -CO_2H$ III, $R = -CH_2OH$

(II)

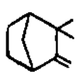
talic acid, has been converted into optically pure α-santalene (I), α-santalic acid (II) and α-santalol (III).

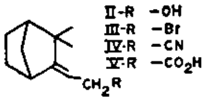
11.5.5 *Synthetic approach in santalene-longifolene series* :

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

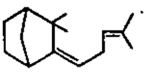
Camphene is converted to the allylic alcohol (II) by Prins reaction. This on bromination, cynation and hydrolysis gave isobicycloekasantalic acid (V). Both the optically active forms of the acid have been synthesised. The acid (V) is being used to synthesise iso-β-santalene (VI) for comparitive odour evaluation in the series. The study of the stereochemistry of the lactone (VII) prepared earlier is in progress.

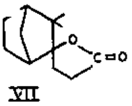
For the synthesis of various derivatives of ∝-and β-santalenes, a large quantity of sandalwood oil has been processed to get (i) saponifiable, and (ii) non-saponifiable parts. The saponifiable part chiefly consisting of acids has been esterified and the mixture of esters separated by chromatography. This mixture is shown to consist of eight components by GLC analysis. The critical examination of the esters is in progress. Two of the constituent acids contain a keto function.


I



II-R $-OH$
III-R $-Br$
IV-R $-CN$
V-R $-CO_2H$


VI



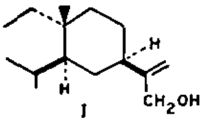
VII

11.5.6 *Base catalysed reactions of lithioethylene diamine* :

This isomerisation has been applied to steroids and medium-sized ring compounds and interesting results have been obtained.

11.5.7 *Selenium dioxide oxidation of terpenes* :

2, 6 Dimethyl octene 2, ∝-santalene, β-santalene, tetrahydro-β-elemene and dihydro-β-selinene gave a mixture of the ∝, β-unsaturated aldehydes and their corresponding alcohols. The mixtures on further reduction gave the alcohols, 2, 6 dimethyl octene-2-o-1, ∝-santalol, β-santalol, the alcohol (I), and dihydrocostol.



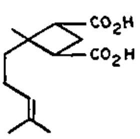
I

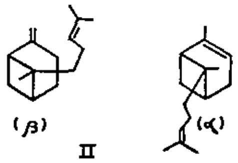
11.5.8 *Bergamotenes* :

The synthesis of *cis*-nor bergamotic acid (I), a key intermediate in the synthesis of ∝-and β-bergamotenes (II) has been described earlier. The synthesis of the model compound pinene (IIIa,b) is carried out using pinic acid (IV, R = H). The diethyl ester (IV, R = CH_3) on acyloin condensation affords a mixture of two acyloins (V). The LAH reduction of the tosylates gave the alcohols, which could be oxidised to the ketones from which nopinone (VI) could be separated and purified by crystallisation of a suitable derivative.

Treatment of nopinone with methyl lithium gives a tertiary alcohol (VII) which on dehydration gives ∝ pinene as one of the products. β–pinene (IIIa) is obtained from nopinone by Wittigs reaction.

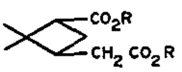
The keto ester (VIII) obtainable from ∝ - pinene by a series of reactions is being converted into the β- diketone (IX) and ultimately to nopinone, and and ∝ and β- pineres.

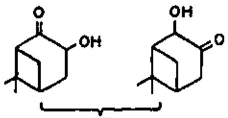

I

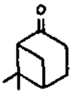

II

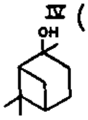

III a

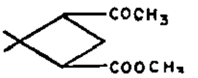

III b

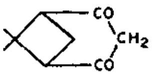

IV (R = H / = Et)


V


VI


VII


VIII


IX

11.6 *Macrocylic musk compounds*

In connection with large scale preparation of exaltone and exaltolide 52 kg. of mustard oil was trans-esterified to get 54 kg. of fatty acid esters. 8 kg. of dihydrxy behenic acid ester and 23.3 kg. sodium paraperiodate are prepared and converted to metaperiodate as required. 8 kg. of dihydroxy behenic acid ester was oxidised with $NaIO_4$ to yield 4.4 kg. of ethyl 12-formyl laurate and 2.5 kg. nonoic aldehyde.

Ethyl 12-formyl laurate was processed further to get diethyl ester of pentadecane dioic acid.

A part of it has been processed to get pure exaltone. So far 281 g. of pure exaltone has been prepared and supplied.

A method for the reduction of acyloins with hydriodic acid in boiling acetic acid has been standardised. 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.

A new method for the preparation of azalic acia semiester has been developed starting from oleic acid.

It has now been found that an aqueous solution of meta-periodate containing sodium nitrate can be used as such for oxidation of 1-2 glycols. This eliminates the necessity of crystallizing meta-periodate.

11.7 *Oxidation of alkyl side-chains in aromatic compounds*

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 and m-tolycarbinyl butyrate.

11.8 *Diethyl-m-toluamide*

Conditions for the preparation of dimethyl-m-toluamide, a useful insect repellent, have been standardized, on ½ kg./day scale in a continuous reactor, using m-toluic acid and diethylamine. The oxidation of m-xylene to m-toluic acid has also been standardized.

11.9 *Sorbic acid*

Sorbic acid is used as a preservative for food, bakery products and chapatis etc. A process for the manufacture of sorbic acid has been worked out on a laboratory scale and about 8 kg. supplied to Defence Food Research Laboratory, Mysore. The quality of this product is generally approved by them. Arrangements have now been made with M/s Sirsilk Ltd., Kagaznagar, for carrying out the first stage of preparation of polyester which involves use of ketene. Based on this product the second stage of synthesis will be investigated at NCL and ultimately it is hoped that M/s Sirsilk will undertake manufacture of sorbic acid.

P.12 PHYSICAL ORGANIC CHEMISTRY

12.1 *NMR studies*

12.1.1 *Aromatic compounds* : The special properties of aromatic compounds have their origin in the nature of the binding of their π-electrons. The question of the presence of double bonds in these systems is closely linked with their " aromaticity ". Other than complete determinatins of structure by X-ray crystallography, the methods available to the chemist for the determination of " bond orders " have been quite limited. Some recent work from this laboratory has shown that measurements of long range spin-spin coupling can be of considerable use in the estimation of bond orders in aromatic compounds.

It has been predicted theoretically that the coupling between benzylic (sp^3) and aromatic protons (benzylic coupling) should vary linearly with the square of the mobile bond order, p, and inversely with $\triangle E$, which is an average electronic singlet-triplet excitation energy. A quantitative verification of the p^2 dependence of benzylic coupling has now been obtained by measurements on a set of closely related methyl substituted aromatic compounds. Indications of the $\triangle E$ dependence have also been obtained. The calculated value of $J_{CH_3-H_{10}}$ for 9 methyl-anthracene agrees well with the observed value[119].

Earlier measurements of benzylic coupling on methyl indanes have been extended to 4-methyl-benzocyclobutene. Comparison of the NMR data obtained with those for benzocyclopropene reveals the interesting manner in which increasing strain introduced by the shorter saturated chains in this series of benzocycloalkenes affects the π- electron distribution in the aromatic ring.

The methyl group which interacts weakly with aromatic rings has been used as a sensing element for studying changes in π- electron distribution brought about by strongly interacting groups like carboxyl and nitro. The data reveal an interesting change in the geometry of the benzene ring which has not been widely recognized. The NMR data are in agreement with the conclusions from X-ray crystallographic work. A satisfactory rationalization of this observation is not yet available. Compounds containing both carboxyl and nitro groups have also been examined. The data obtained are under analysis.

12.1.2 *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 in the last few years.

A number of fairly stable oxo-carbonium salts have been prepared in the pure solid state and their NMR spectra studied (in solution). The data obtained are of considerable interest and may lead to new information on barriers to rotation in conjugated carbonium ions.

The possibility of obtaining unambiguous evidence for a truly non-classical oxo-carbonium ion is being actively pursued.

Since there are strong reasons to doubt the reported stability of some allyl carbonium ions to internal rotation, a reinvestigation of these systems has been undertaken and the necessary derivatives have been prepared.

12.1.3 *Intermolecular interactions* : The distribution of isomers in aromatic halogenation is influenced substantially by the solvents used. A PMR spectroscopic study of the interactions of toluene with various solvents was undertaken with the hope that it would help clarify the nature of these solvent effects. The results obtained show that the variation of selectivity with solvents, observed in the chlorination of toluene, may be adequately accounted for by interactions of the substrate with solvent. The suggestion made earlier that changes in selectivity are due to the interactions of chlorine with solvents is shown to be unsound.

12.1.4 *Stereochemical correlations* : It has been observed in a few cases that a carbonyl group of a carboxylic acid or its ester shields a methyl group which has a 1, 3-*cis* diaxial relation with it. It has now been found that this effect is general, and the carboxylate anion deshields the same methyl group. Using these two effects and also finding the shifts of the methyl group attached to the carbon bearing the carboxyl group in a number of model compounds, a method has been devised to find : (i) whether a carbon bearing a carboxyl group also bears a methyl group on it (ii) the conformation of this methyl group (iii) the conformation of the carboxyl group, and finally (iv) the stereochemistry of the fusion of the ring holding the carboxyl group with the neighbouring ring[58].

Using the above novel NMR techniques the stereochemistry of two diterpene acids, salvin and picrosalvin have now been determined. Their absolute configuration has also been formulated from rotational data.[59]

12.1.5 *Signal identification* : The usual method to identify the proton or protons on a carbon bearing a hydroxyl group is to acetylate, or in general to esterify the hydroxyl group when the proton or protons concerned moves downfield by about 0.5 to 1.5 τ units. However, this procedure may not always be convenient either due to interferring protons in the regions or due to other reasons. An alternate method is now formulated for the purpose. By taking a variety of model compounds it has been found that if the hydroxyl group is methylated, this proton on a secondary carbon not having an adjacent double bond, moves up field by about 0.6 τ units. Other signal correlations are also formulated[60].

12.1.6 *Conformation of ring A in terpenoids* : Many sesqui--, di--and tri-terpenoid compounds contain a gem dimethyl group at C_4. In some cases one of these methyl groups is oxidised to a primary hydroxyl or aldehyde or acid. In some cases further oxidation has taken place at C_6 to give a hydroxyl or an ester group. Generally it is assumed that in all these cases ring A exists in the chain conformation. It has now been found from terpenes, studied in this laboratory and from a critical examination of literature that in normal A/B trans-terpenoids devoid of a C_3-equatorial hydroxyl group, if the gem diethyl group or its equivalent at C_4 would have 1,3, *cis*-diaxial interactions with a C_{10} axial methyl group and a C_6 equatorial or equatorial-like substituent, then the ring A of the compound will adopt a flexible conformation so as to get some relief from the non-bonded interactions involved[64].

12.2 *Mills-Nixon effect and allied problems*

The Mills-Nixon effect is a problem in the structural theory of organic compounds that has been under debate ever since 1930. It concerns the extent and direction of fixation of π- bonds in indane and tetralin. Since some very basic notions of structural theory are involved in this question, investigations that seek a final answer to it can be very rewarding.

A recent NMR spectroscopic study from this laboratory has shown that the mobile bond order of the 4-5 bond of indane is larger than that of the 5-6 bond indicating localization of π- bonds in a sense opposite to that suggested by Mills and Nixon. Confirmatory evidence is now sought from an examination of the nucleophilic reactivity of the aromatic ring of indane.

Studies are also in progress to relate the reactivities of functional groups in the alicyclic part of the molecule to the stress-strain analysis of Coulson and Longuet-Higgins.

12.3 *Mass spectrometry*

In view of the proposed installation of double focussing mass spectrometer, CEC21-110B, in April 1966 and for initiation of work in mass spectrometric applications in organic chemistry, about a dozen samples of carbohydrate derivatives, triterpenes and anthraquinone derivatives were sent to different laboratories in USA for mass spectral analysis. Spectra obtained were interpreted and the results sent for publication.

Further investigations were undertaken to generalise our recent reports on skeletal rearrangements of organic molecules under electron impact involving the migration of groups heavier than hydrogen. Various carbonyl derivatives were prepared in pure form and they were also sent to two institutes in USA for obtaining their mass spectra. The interpretation of these spectra gave evidence for the migration of amino groups under electron impact. The results have been sent for presentation on behalf of the authors at the 14th Annual Conference on Mass Spectrometry and Allied Topics held in May 1966 at Dallas—Texas, USA.

Study of the biogenesis of Aflotoxin has been undertaken using (^{13}c) labelled precursors and spectral methods.

12.4 *Polyesters as stationary phases in GLC analysis*

The effect of spacing of methylene groups in dicarboxylic acid fragment is being studied. The spacing of methylene groups in glycolic fragment has been critically examined and the relation found to be linerar.

The constant 'C' in the formula

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

is different from the constant 'C' for the spacing of methylene groups in dicarboxylic acid fragment of the polyester.

Next, the effect of the molar proportions of these polyesters has been investigated. It was observed that molecular weight does not have appreciable influence on the separation. However, during these studies it was found that the contribution per gram per methylene group remains the same.

On the basis of these results, it is now possible to prepare tailor-made polyester stationary phases for specific separations which hitherto have not been found feasible.

P. 13 MICROBIOLOGY

13.1 *National collection of industrial microorganisms.*

The culture collection consists of about 1200 nonpathogenic 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 were carried out. 634 cultures were distributed on request to industrial concerns and research institutions.

13.2 *Microbiological oxidation of hydrocarbons*

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 was undertaken. Three cultures were 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.

13.3 *Metabolism of C_5 — dicarboxylic acids*

C_5 — branched chain dicarboxylic acids such as itaconic acid, mesaconic acid, and citramalic acid are known to occur in nature.

Attempts were made to characterise other *cis-trans*-isomerases. Work on citroconate revealed the presence of a new enzyme—citraconase, which has been found to be a hydrase instead of a *cis-trans*-isomerase, converting citraconic acid into (±) citramalate acid. The mode of addition of water to citraconic and masaconic acid by the enzyme has been studied. Citraconase is activated by addition of and incubation with Fe^{2+} ions and a reducing agent. The properties of the enzyme and the kinetics of the reaction are being studied.

Similar work on the C_4—dicarboxylic acid maleate has been undertaken.

13.4 *Bacterial diastase*

Tests on the stability and performance of the culture used for the bacterial diastase process were carried out. Assistance was rendered to the firm, to which the process has been leased, in testing filter aid and antifoam agents and in demonstrating the process to its staff member.

13.5 *Microbiological transformations of terpenes*

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

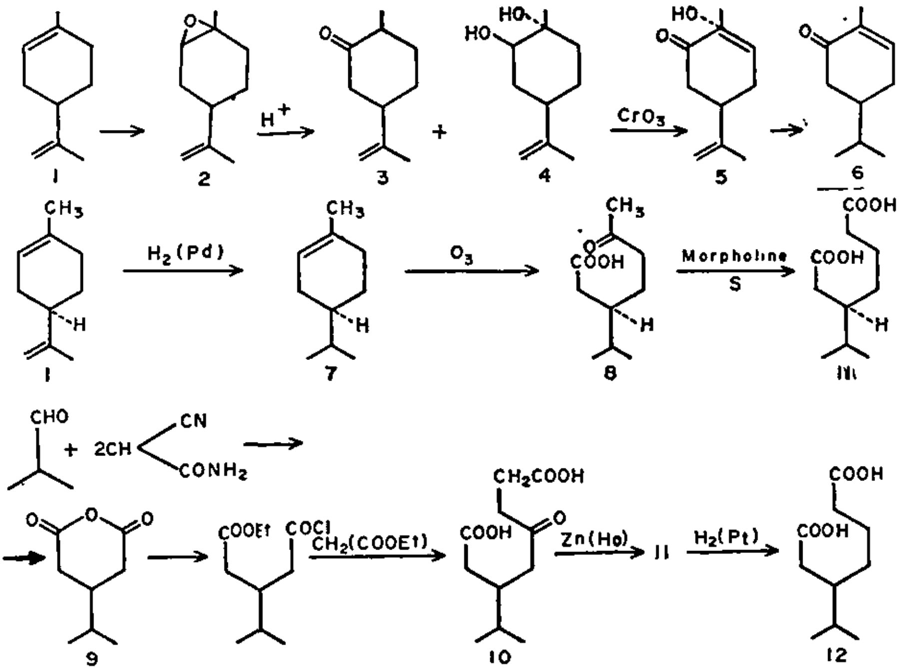
Earlier studies had indicated that fungi and bacteria bring about in these compounds chemical changes such as hydroxylation, hydration, oxygenation on double bonds, oxidation of the functional groups and carbon-carbon bond cleavage.

13.5.1 *Fungal transformations : Mechanism of fungal hydroxylation* : A strain of *Aspergillus niger* (NCIM 612) is found to carry out stereospecific allylic hydroxylation in a large number of substrates giving rise to optically active products viz. verbenol, verbenone and others. In certain cases, however, racemic products such as 2-hydroxy-1-methyl cyclohexene and ∝ — tetralol were obtained. This preservation or failure of stereospecificity is explained by " hot " carbonium ion mechanism[93]. Further studies are in progress to determine whether the hydroxy oxygen is derived from atmosphere or from the medium.

13.5.2 *Bacterial transformations* :

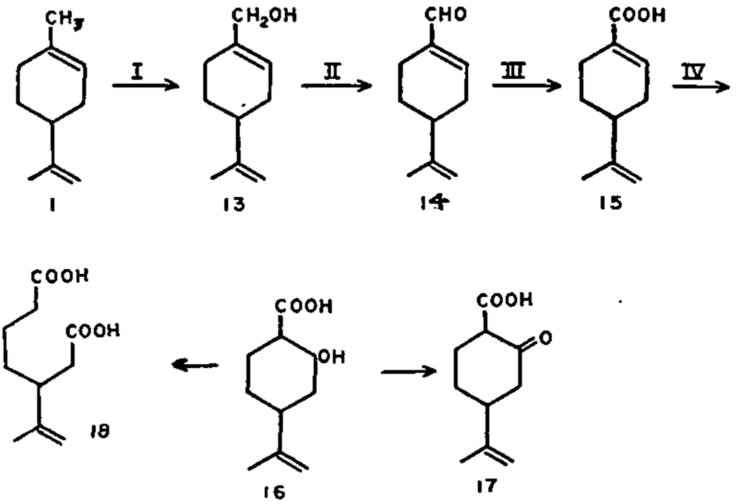
13·5·2·1 *Fermentation of limonene* : Limonene (I) on fermentation with pseudomonad was found to accumulate the following compounds : carveol, carvone, dihydrocarvone, 8-p-menthene-1, 2-transdiol,8-p-menthene-1-o*l*-2-one, 8-p-menthene-1, 2-*cis*-diol, 1-p-menthene-6,9-diol, perillic acid, 2-hydroxy-8-p-menthene-7-oic acid, *β*-isopropenyl pimelic acid and 4, 9-dihydroxyphellandric acid.

(*a*) *Synthetic studies* : Synthetic studies to determine the structure and stereochemistry of some of above produts were undertaken (+) Dihydrocarvone (3), 8-p-menthene-1, 2-trans diol (4),8-p-menthene-1-ol-2-one (5) and carvone (6) are synthesised from limonene-1, 2-oxide (2).



The structure of β-isopropylpimelic acid (11) and-β-isopropenyl-pimelic acid (12) are established by their total synthesis.

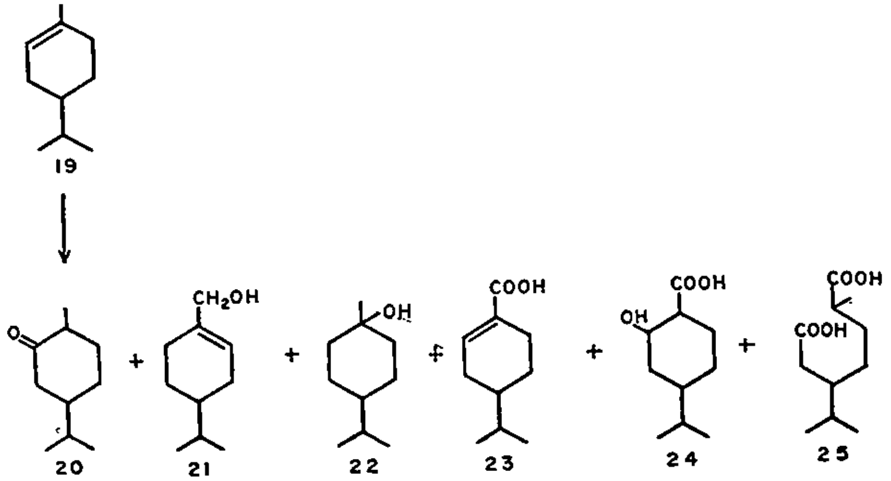
(*b*) *Enzyme studies* : All the enzymes responsible for the oxidation of limonene (1) to the dicarboxylic acid (18) in the following pathway have been demonstrated.



The hydroxylating enzyme (I) carrying out the hydroxylation of limonene (1) to perillyl alochol (13) was present in the 100,000 × g. precipitate from the sonicate.

Perillyl alcohol dehydrogenase (II) carrying out dehydrogenation of perillyl alcohol (13) to aldehyde (14) was found to show some interesting steric requirements, and was present in the cell-free sonicates. It was purified 7-8 fold by ammonium sulphate fractionation and calcium phosphate gel chromatography. Further purification (18-25 fold) has been carried out, but the enzyme becomes unstable. Kinetic study of this enzyme has been completed. Studies on the next enzyme, perillyl aldehyde dehydrogenase (III) which brings about the dehydrogenation of perillyl aldehyde to pimelic acid are in progress. The formation of dicarboxylic acid (18) from (15) could be demonstrated in the supernatant in the presence of CoA-SH, ATP, Mg^{+2} and NAD[92,93]

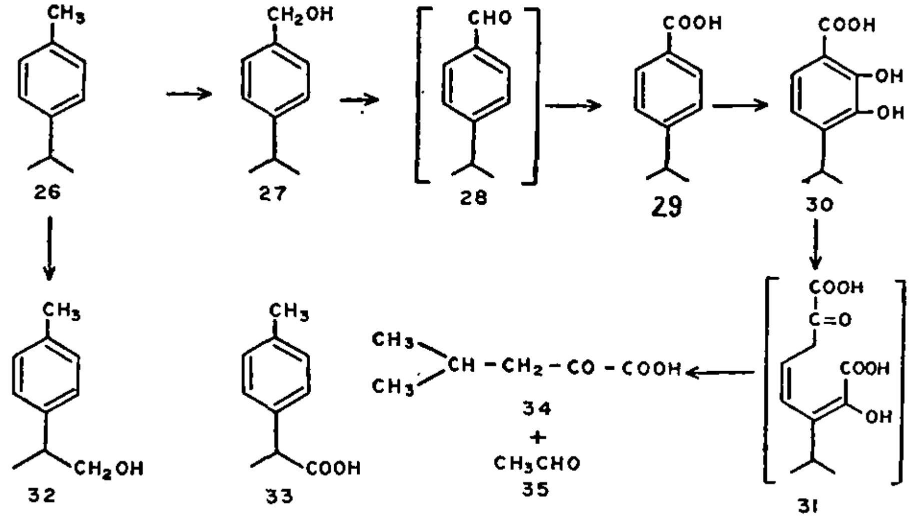
13.5.2.2 *Fermentation of 1-p-menthene* : It was reported earlier that a major pathway of degradation of α-and β-pinenes in PL strain involved a p-menthenoid intermediate. It was considered desirable to study the fermentation of 1-p-menthene (19). Amongst the fermentation products tetrahydrocarvone (20), phellandrol (21), p-menth-1-ol (22), phellandric acid (23), 2-hydroxy-p-menth-7-oic-acid (24) and β-isopropylpimelic acid (25) were isolated.



It was observed that β-isopropylpimelic acid (25), accumulated in major quantity when the fermentation was carried out for 48 and 72 hrs. while the 24 hr., fermentation did not yield any dicarboxylic acid. Glucose grown cells were converted (19), to phellandrol (21), and to a small amount of phellandric acid (23). Growth and adaptive studies are in progress.

13.5.2.3 *Fermentation of p-cymene* : In continuation of our observation on the metabolism of α-and β-pinenes and limonene by a soil pseudomonad, the studies on metabolic fate of p-cymene as a substrate (26) was undertaken. Among the metabolites, cumic acid (29), p-tolylpropionic acid

(33), 2:3 dihydroxycumic acid (30) and isopropyl pyruvic acid (34), were isolated as acidic products, and cumic alcohol (27), 9-hydroxy-p-cymene (32), and acetaldehyde (35), as neutral products. Incubation of cell-free extracts with (30), yielded isopropyl pyruvic acid (34), and acetaldehyde (35), isolated as their 2, 4-dinitrophenylhydrazones.

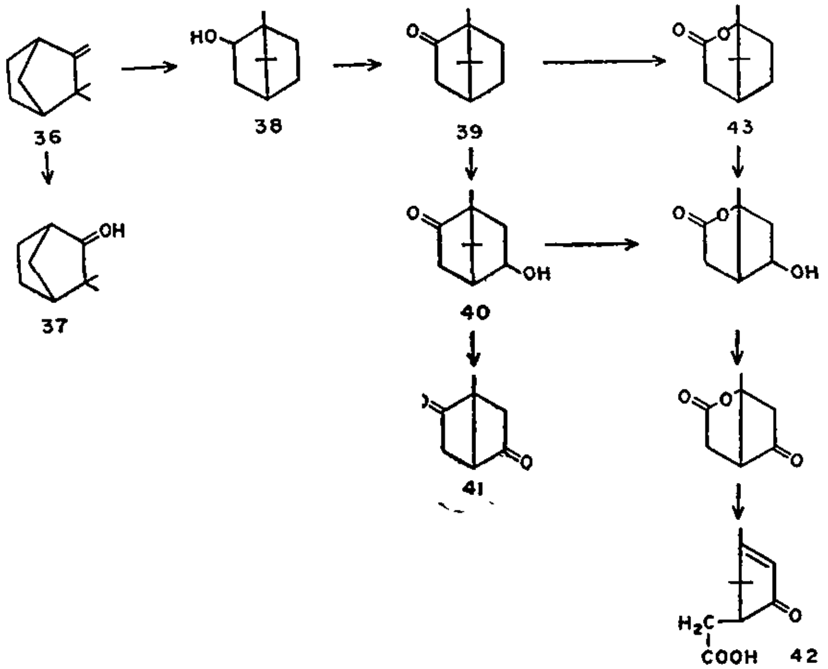


Adaptive enzyme studies and growth studies indicated that p-cymene-grown cells oxidise (27, 29, 30), but not 2-hydroxy or 3-hydroxy cumic acids. Cell-free extracts contain an oxygenase that brings about the metapyrocatachase type reaction to give an hypothetic keto acid (31), which undergoes cleavage to isopropyl pyruvic acid (34), acetaldehyde (35) and another unidentified two carbon fragments.

From these observations it is concluded that the pathway of degradation of p-cymene to cumic acid is similar to that observed with limonene, 1-p-menthene and ∝-and β-pinenes with the exception, that in the former case instead of hydration a dioxygenation reaction takes place leading to a dihydroxy acid.

13.5.2.4 *Fermentation of camphene* : A pseudomonad (different from the PL strain) hereafter designated as the camphene strain has been isolated by enrichment culture technique. Among the fermentation products of camphene (36), by this strain, camphenilone (37), isoborneol (38), camphor (39), 5-exohydroxy-camphane (40), 2, 5-diketocamphane (41) and 1, 2-campholide (43) have been identified as neutral products and 3, 4, 4-trimethyl-5-carboxymethyl-Δ_2-cyclopentenone (42) as the acidic product.

It is established that this strain converts camphene to isoborneol by a prototropic rearrangement. Isoborneol is then dehydrogenated to camphor, which is then metabolised by, if not the same, a closely similar pathway followed by the camphor fermenting pseudomonad, C_1 and C_5.



The enzyme bringing about the prototropic rearrangement of camphene (36), to isoborneol (38), has been demonstrated in the sediment. The alcohol dehydrogenases that brings about the conversion of (38) to (39) and (40) to (41) and the lactonising enzyme which brings about the conversion of (39) to (43) have been demonstrated in cell-free extracts.

A programme has been undertaken with the University of Illinois to make a comparative study of this camphene strain with the C_1 and C_5 strains.

P. 14 GROWTH OF PLANT CELLS

The objective of this project 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.) were determined in previous years. Twentyfive plant cells cultures are being maintained at present, of which some were isolated and established as viable *in vitro* cultures for the first time in this laboratory. The main objectives at present are (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.

Subculture of maize callus tissue isolated in this laboratory was continued in order to determine its viability on continuous maintenance *in vitro*. The effect of other constituents such as sugars, nitrogen sources and mineral salts on the growth of the culture were studied. Glucose was found to be less effective than sucrose in supporting the growth of maize cells. Diphenylurea was found to stimulate growth whereas several other compounds which were tested such as zeatin and kinetin were found to have no effect on the growth of the cells[95].

Comparative studies on normal and crown gall tissue of parthenocissus were continued. There was no significant difference in the lactic dehydrogenase and the hexokinase of the two tissues but a lactic dehydrogenase inhibitor was found specifically to inhibit tumour growth. 700 gm. of the crown gall tissue were grown and the lipids were isolated. Characterisation and estimations of the ubiquinone of normal and tumour tissues were carried out and it was found that both of them contained the isoprenologue Q_8.

Studies on the optimum conditions for obtaining single cell cultures with different tissues are in progress since media for the growth of larger pieces of tissue (10-50 mgm) were unsuitable for the growth of single cells.

P. 15 ENZYMES

15.1 *Hexokinase*

Animal tissue hexokinases have not hitherto been obtained in pure form. A new method for the solubilization of the particulate hexokinase of brain was discovered and work on the purification of this enzyme, which plays an important role in carbohydrate metabolism, is in progress.

Purified hexokinase was extremely unstable and further purification was not possible until it was discovered that high concentrations of glucose or fructose stabilise the enzyme even at high temperatures. The enzyme was then purified by DEAE cellulose chromatography and ammonium sulphate fractionation to a final specific activity of about 50 units/mg protein. Ultra-centrifugal studies indicated one major component and two minor components and the major component which constituted about 85 per cent of the total protein was isolated in a partition cell and shown to be hexokinase. Kinetic studies on K_m for glucose, ATP and Mg were carried out. Interaction of the enzyme with glucose-6-phosphate, which inhibits it and inorganic phosphate which reverses the inhibition, is being studied, using a new method of assay. The purification of the muscle tissue hexokinase which is present in relatively smaller amounts than in brain is in progress.[120]

15.2 *Phytase*

A new bacterial enzyme which specifically hydrolyses inositol hexaphosphate is under study. The purification of the enzyme and the study of its properties and specificity has been undertaken.

Chromatographic methods for the purification and isolation of phytase and of the products of the enzymic hydrolysis of phytate were standardised and a large scale isolation of the reaction product was carried out. It was shown that three moles of inorganic phosphate were liberated from one mole of phytate and the ratio of phosphateto inositol in the reaction product wasfound to be 3 : 1. The product is probably a symmetrical inositol triphosphate since it showed no reaction with periodate. Nucleotidase activity present in the enzyme was shown to be different from the phytase since it was not found to require calcium unlike phytase. Studies with p^{32} showed no uptake of radioactive inorganic phosphate in the presence of enzyme and phytate.

15.3 *Acetylcholinesterase*

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 electric organs of some fish. A new method has been worked out for the preparation of soluble acetylcholinesterase from ox brain. Both brain as well as caudate nucleus were used for enzyme isolation but further purification was carried out with the latter owing to its much greater enzyme content. The soluble enzyme was shown to be a true acetylcholinesterase. It was purified about 40-fold by DEAE chromatography and the kinetics and properties and further purification of the enzyme are being studied.

15.4 *Brain DPNase*

This enzyme which splits DPN and TPN at the nicotinamide ribose link has been obtained for the first time in soluble form from beef brain and spleen. The enzyme from these sources is different from the DPNase from other animal tissues, in being sensitive to isonicotinic acid hydrazide. Attempts to demonstrate other DPNases which are specific for TPN or hydrolyse the nucleotides at the pyrophosphate link were unsuccessful. Ox brain DPNase was found to be unusually acid stable and work on its isolation is being continued. Preliminary work was also undertaken on a soluble ATP hydrolysing system from brain.

15.5 *Nitrate and nitrite reductase*

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

The present investigation has been undertaken to elucidate the mechanism of nitrate and nitrite utilisation by the luminous bacterium *Achromobacter fischeri.*

The formation of nitrite reductase by *Achromobacter fisheri* was demonstrated for the first time in this laboratory. This is contradictory to the conclusion reported earlier by McElroy, et al [*Archiv. of Biochem. Biophys.* **67**, 16, (1957).] that *A. fischeri* can form inducible nitrate reductase but no nitrite reductase. The procedure for purification of nitrite reductase from *A. fischeri* was standardised and the sequence of electron transport for nitrite reduction worked out.

Conditions for the growth of *A. fischeri* with a view to obtaining high yields of nitrite reductase as well as enzyme with a higher starting specific activity were worked out. The enzyme was obtained in an ultracentrifugally homogeneous state with an s_{20}, W value of 5.2. The pH optimum for nitrite reduction was between 7.4 to 7.6 and the K_m for nitrite was 4.1×10^{-5} M. Cyanide (10^{-3} M) and CO (1 atm., in the dark) completely inhibited the enzyme. Inhibition by CO is reversed by light. The purified enzyme showed absorption peaks at 280, 409 and 525 mu in the oxidized form and at 420, 522 and 551 mu in the dithionite-reduced form. The spectrum of the reduced form of the enzyme reverted to that of the oxidized state immediately on addition of O_2 or of KNO_2 under anaerobic conditions but not of KNO_3.

From these findings, it has been concluded that nitrite reductase from *A. fischeri* is an haem-containing protein with only a c-type spectrum in contrast to the enzyme from Pseudomonas whch is reported to contain two haems, have a_2 and c-type haem on the molecule.

Further studies on nitrate metabolism by *A. fischeri* are continued with a view to collect sufficient quantities of purified nitrite reductase for determination of molecular weight, haem content and for study of other physico-chemical properties.

15.6 *Citrate-oxaloacetate lyase*

The induction of citrase, the enzyme which cleaves citrate to oxaloacetate and acetate, takes place in cells of *Aerobacter aerogenes* grown on citrate. The enzyme has been purified and the application of the pure preparation to a rapid, accurate and sensitive spectrophotometric assay of citrate has also been developed.

Studies are in progress on the mechanism of enzyme action and the location of active sites on the enzyme molecule. Citrase is rapidly inhibited by oxaloacetate, a product of the enzyme action through formation of a stable product-enzyme complex. Conditions for the formation of the complex and release of enzyme from the complex have been established. The chemical reduction of the product-enzyme complex is now being studied.

15.7 *∝-Amino acid acylases*

Enzymes of the class ∝-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 a new fungal enzyme isolated from *Aspergillus flavus-oryzae* have been studied. The enzyme differs in its substrate specificity and metal requirements from those hitherto reported in literature for this group of enzymes. The purified enzyme acts on aromatic amino acid derivatives like other microbial acylases and unlike renal acylase. The enzyme shows unique metal requirements; Zn^{2+} or Fe^{2+} being required for its activity, while Co^{2+} is without effect.

P. 16 PHYSICO-CHEMICAL STUDIES OF POLYMERS

16.1 *Solution properties of polymers*

In examining the applicability of the single parameter method of molecular weight determination of polymers from their solution viscosities, the studies have been extended to poly p-chlorostyrene, randomly branched polyvinyl acetate and azeotropic copolymer of p-chlorostyrene and methyl methacrylate. The ordinate $[\eta]_R$, at the common point of convergence of the In η_r/C vs C plots correlates well with the square-root of molecular weight in all these cases as in the case of polystyrene, polymethyl acrylate and linear polyvinyl acetates reported earlier [*J. Polym. Sci.* 57, 373 (1962)]. For polyvinyl acetate, both linear and randomly branched, the unperturbed dimensions are found to be dependent on the specific nature of the solvent and higher in non-polar solvent. The values of $[\eta]_R$ obtained are independent of the nature of the solvent used.

Examination of the solution behaviour of high conversion (randomly branched) polyvinyl acetates, indicates that (a) the expansion of the branched polymer in solution over its unperturbed dimensions is not very different from that of the linear sample, (b) the branching parameters estimated from the kinetic chain transfer constant C_p are in agreement with those obtained from measured dimensions (c) the branching parameters obtained from viscosity measurements are lower in good solvents and higher in poor solvents, and (d) good estimates of branching are obtained from $[\eta]_R$ using Zimm-Kilb theory at lower branching frequencies and Zimm-Thurmond relationship at lower branching frequencies.

The solution behaviour of fractions of an azeotropic copolymer of methyl methacrylate and p-chlorostyrene has been examined by viscosity and light scattering techniques in benzene, chloroform, dioxane and two theta solvent mixtures. Corrected weight-average molecular weights have been obtained by the extrapolation method of Stockmeyer et al. It is observed that the unperturbed dimensions of the copolymer are uninfluenced by the specific nature of the solvent. Results obtained with poly p-chlorostyrene and literature data on polymethyl methacrylate indicate that the copolymer in solution is extended to an approximate extent of 6 % over either of the two homopolymers under random flight conditions.

16.2 *Stereospecific polymerization*

The polymerization of stryrene with $Z_r Cl_4$ in combination with Al (i) Bu_3 and $VOCl_3$ in combination with Al (i) Bu_3 at 40° in presence of toluene and n-hexane, has been investigated. The rate of polymerization was found to be first order in respect of monomer and catalyst concentration for the first system whereas the rate of polymerization varied linearly with monomer and bimolecularly with catalysts in the second system. The activation energy for the first system was found to be 14.5 Kcal/mole and 11.5 Kcal/mole for the second system.

Following these studies, catalyst systems using $ZrCl_3$ with Al ($C_2 H_5$ $)_3$ and Al (i) Bu_3 were tried. The rate of polymerization was found to be dependent on second order of catalyst concentration and first order of monomer concentration. The second order dependence of catalyst concentration suggests that in both the cases two different catalyst systems are involved for the formation of the polymer. Activation energy for the two systems was 10 and 6 Kcal/mole, which may presumably be due to their structural changes. Molecular weight of the polymer in both the cases was higher than that obtained with the corresponding $ZrCl_4$ systems. Besides, the fraction of the polymer was insoluble in usual solvents at room temperature, which also suggests crystalline nature of the polymer formed.

Polymerization of acrylonitrile was conducted with $VOCl_3 - Al(C_2H_5)_3$ catalyst system at room temperature in n-hexane. The polymer obtained was partially dissolved in dimenthyl formamide when extracted with the solvent on soxhlet apparatus. The soluble fraction so obtained is being characterised. The product as a whole when examined by infra-red absorption spectrum showed partial cyclisation. This is being further examined. It is reported that copolymer of styrene and acrylonitrile yields a high melting transparent product with improved impact resistance. Preliminary study in this connection has been carried out with small percentage of acrylonitrile using the above catalyst system.

16.3 *Telomerization*

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 telomerization of ethylene with carbon tetrachloride, and the required type of telomer is formed at 105° and 90 to 100 atms.

16.4 *Polymerization of turpentine fractions*

The Indian turpentine oil contains a large proportion of Δ^3–carene and hence does not find proper industrial application. A large quantity of Δ^3–carene is also available as a by-product from camphor industry. With a veiw to find useful application of Δ^3–carene, some studies on its polymerization have been initiated.

Polymerization of Δ^3–carene with BF_3 has been investigated under various conditions. A typical analysis of the reaction product shows the presence of about 16-18% of an isomeric raction containing p-cymene and probably m-cymene, 55-60% mostly dimer with a small amount of trimer and 10-18% of a higher polymer containing mostly trimers and tetramers. The dimer, which is the major product of this reaction, is resistant to further polymerization. Its use as a plasticizer for PVC is being examined.

A few preliminary experiments on the polymerization of Δ^3–carene using Ziegler catalyst systems (a) $TiCl_4$-$AlEt_2Br$, (*b*) $VOCl_3$ and $AlEt_3$ and (c) $ZrCl_3$-$AlEt_3$ at room temperature have been carried out. A yellow coloured solid product was obtained with the first and third catalyst systems whereas a resinous material was obtained with the second catalyst system.

16.5 *Degradation of long chain molecules by ultrasonics*

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 to industry.

Work was continued on the degradation of butyl rubber solutions. The results of degradation were studied by two different methods, one by solution viscosity method and the other by estimating free radicals as a function of DPPH consumed. It has been observed that the general shape of the two curves are similar but not identical. 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 carrried out. The ultrasonic degradation under experimental condition is primarily due to hydrodynamical forces arising from cavitation of fluid and cavitation intensity varies with viscosity of solution, hence scission of molecules is reduced with increase in viscosity of the solutions. Further the degradation rates in the two solvent media having initially the same viscosity, have been found unequal. A possible explanation is that since viscosity along with the cavitational intensity changes at different rates during the course of degradation, the degradation rates in the two cases would be unequal. The initial viscosity of the degradating solution has been found to control the final value of the degree of polymerization, $\overline{(\mathrm{DP})}_{\propto}$.

P. 17 ION EXCHANGE RESINS

17.1 *Improved styrene-DVB cation-exchange resin*

Conditions for the copolymerization of styrene-DVB using different inert solvents have been standardized on 15 kg. batch. The physical attrition resistance of the improved resin is found comparable to similar imported products. Modified techniques have also been introduced in the sulphonation and washing steps.

A large quantity of the resin has been distributed to several research laboratories in the country for trials and evaluation. The resin has been found suitable for water treatment, amino acid separation and in the recovery of pectins from citrus peels.

Recovery of some of the by-products formed during the sulphonation step, is being examined. For a systematic evaluation of the improved resin, a column study has been initiated.

17.2 *Styrene-DVB anion-exchange resins*

Chloromethylation of the styrene-DVB copolymer having different degree of cross linking was studied in detail and optimum conditions have been established.

When trimethylamine was used for amination a resin with a capacity of 3.8 - 4.1 meq/g was obtained which is comparable with a similar imported product.

With the use of dimethylaminoethanol for amination a resin with 3.3 meq/g capacity could be obtained.

17.3 *Electrodialysis with ion-exchange membranes*

Using indigenous ion-exchange resin cation and anion exchange membranes were prepared with the help of M/s Swastik Rubber Products, Kirkee. These membranes were used in a frame-work prepared in NCL workshop to set up a bench-scale electrodialysis unit. Desalination experiments were conducted with this unit using sea water. Seven cell pairs were used and the extent of desalting was about 25% in one cycle at the rate of about 1 litre/hour. This project has now been transferred to Central Salt & Marine Chemicals Research Institute, Bhavnagar.

17.4 *Preparation of porous ion-exchange resins*

Preliminary work was started to prepare porous polymers by suspension polymerization using selected solvents. Using these solvents as diluents, several samples of styrene-DVB copolymers were prepared with different degrees of cross-linking. These were studied for their density and toluene swelling ratio and compared with the conventional resins. These polymers were sulphonated and their cation-exchange capacities determined.

17.5 *Column studies on cation and anion-exchange resins*

A cation-exchange resin prepared from styrene and furfural was studied for its column performance under different conditions of operations. The breakthrough capacity obtained was of the order of 24-28 kg $CaCO_3/m^3$.

Similarly, a modified anion-exchange resin from melamine and formaldehyde was also studied in columns under various conditions of operations and the capacity and regenerant dosage etc. were determined. The breakthrough capacity obtained in this case was of the order of 50 kg CaCO /m^3.

17.6 *Catalysis by ion-exchante resins*

Some preliminary work has been undertaken on esterification reactions using ion-exchange resins as catalysts. The results obtained are encouraging and the various resins and systems are under investigation.

18.1 *Polystyrene foams*

Suspension polymerization of styrene incorporating low boiling petroleum fractions so as to obtain free flowing expandable beads, has been continued. The time of polymerization has been reduced from 32 hours to about 25 hours and conditions have been standardized to obtain the required optimum degree of polymerization The factors influencing size and size-distribution of the beads are being studied to obtain 0.9 mm beads as the major fraction; yield of this fraction is about 50%. The beads obtained show an expansion of 40-50 times of pre-expansion with subsequent slight shrinkage. A small size continuous pre-expander has been designed and it is under fabrication.

18.2 *Rigid sand filters*

Active assistance was rendered to M/s Ashim Filters, Allahabad, to whom the process for the manufacture of rigid sand filters has been released, during the initial stages of the start up of their factory.

Large quantity of phenolic resins has been prepared and utilized for the preparation of two sand filter slabs each measuring 24″ × 24″ × 3″. One of these slabs has been sent to Bombay Municipal Corporation for filtration trials.

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

18.3 *Polyurethanes*

Polyurethanes are polymers of comparatively recent origin, which are finding increasing applications in various industrial fields. Chemically these polymers are formed by reacting polyhydric materials with polyisocyanates and show a wide range of properties.

18.3.1 *Typewriter rollers* : Formulations for the preparation of typewriter rollers of specified properties based on polyurethanes and on liquid rubber have been developed. Work on standardization of casting and on moulding techniques of these rollers has been undertaken.

18.3.2 *Adhesives* : Polyisocyanates containing phosphorus and triazine ring have been synthesized and adhesive formulations using them are being standardized.

Polyurethane based adhesives of the above type are employed in rubber, leather, aircraft and automobile industries.

18.3.3 *Evaluation of castor oil for the preparation of polyurethane elastomers* : Dihydroxy compound prepared from castor oil has been reacted with different isocyanates and the properties of resultant gums are being studied with a view to prepare cheap elastomers.

18.3.4 *Coatings* : At the initiation of SASMIRA, Bombay, polyester polyisocyanates based coating compositions for nylon fabric were developed. Modifications are being introduced to suit the exact requirements of SASMIRA.

The polyurethane coated nylons find large applications in the manufacture of light weight rain coats, high altitude huts and wind socks on aerodromes.

18.3.5 *Binder for composite propellants* : A castor oil-based formulation for making composite propellants was developed and samples were sent for trials. On the basis of the suggestions received, some new formulations are being attempted.

P.19 SURFACE COATINGS

19.1 *Styrenated alkyds*

Test reports received from various parties on alkyds prepared in the laboratory suggested the desirability of reducing the drying time of resin and attempts have been made to improve the same. A satisfactory composition of the alkyd resin based on high and medium oil length has been found to meet the requirements in all respects and about 10 kg. of the modified styrenated alkyd was prepared. Films of the resin solution (50% N. V) dry in less than 5 minutes and become tack-free in less than 30 minutes. Samples of these resins were supplied to 5 parties for trials, and test reports received so far are quite satisfactory. Steps are being taken to prepare the resin on a large scale so as to collect necessary data for cost evaluation and for release of the process for its commercial exploitation.

19.2 *Linseed oil emulsion*

Attempts to prepare surface coatings from linseed oil emulsion are continued. Linseed oil was bleached, refined and later bodied under vacuum. Emulsions from the resulting product were found to separate on storage. The procedure of bodying the oil is being modified to obtain a stable emulsion with good film properties.

19.3 *Chemical modification of lac*

The object of this investigation is to improve the physical and chemical properties of the shellac films. In the present work, the film properties were studied for a few compositions made by reacting different types of short and long chain polyols like glycerol, diethylene glycol, butanediol, trimethylol propane and polyethylene glycol (PEG) with toluene di-isocyanate (TDI) using *dioxane and ethyl acetate as solvents. These polyol isocyanate intermediate* products were reacted with phenol to block the NCO groups and finally combined with shellac solution to give the coating composition. It is applied as a thin film and cured at 150° for one hour, during which OH groups of lac react with the liberated NCO groups resulting in a cross-linked material. Of the various compositions studied, the one made from glycerol, PEG, TDI and shellac gave improved film properties viz. adhesion, hardness, flexibility and was unaffected by water, acids like 30% sulphuric, 30% hydrochloric, 5% acetic, 5% citric, 5% tartaric; 5% salt solution, 10% sodium hydroxide solution and solvents like ethyl alcohol, benzene, xylene, carbon tetrachloride, for more than 15 days. However, the films were affected by acetone and methyl ethyl ketone. Further, this coating composition possesses excellent shelf life.

The suitability of these baked coatings for various applications are being examined for the development of air dried coatings.

19.4 *Coating for steel tapes*

After receiving report on the steel tapes coated in 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 performance is awaited.

P. 20 RUBBER

20.1 *Modified rubber*

Large quantity of modified rubber was prepared from natural rubber latex and its physical properties (tensile, modulus, ageing etc.) were determined. The results indicate that the incorporation of proteins improves the physical properties; tensile strength and modulus increase by about 3 times over that of pale crepe. This procedure could be adopted at the site of the collection of rubber latex. Results of these investigations are being published.

20.2 *Rubberised cork-sheets*

Rubberised cork-sheets are used as gaskets in automobiles, oil engines and in similar equipment. Systematic study on the incorporation of cork granules into natural and synthetic rubbers so as to obtain sheets with good tensile strength, compression set, age resistance, resistance to shrinkage and with standard hardness number of 45-65, was carried out. Rubber is used as a binder, and it is incorporated into the cork granules without affecting their physical characteristics. Conditions for the preparation of the sheets have been standardised and preliminary tests on their usage were quite encouraging. About 15 sheets of 18″ × 18″ in different thicknesses have been sent for service tests and results are awaited. The process will be shortly released for its commercial exploitation.

20.3 *Sponge textiles*

Latexf-oam backed textiles are finding extensive use in various fields such as floor covering, carpets, upholstery etc.

A spreading machine suitable for this work has been fabricated. Trial runs have been taken and a few more modifications in doctor blade, heating block and winding roll are found necessary in the machine to obtain foam of uniform porosity and with foam ratio of 1·3–1·5. A few lengths of textile material was coated with foamed latex. Further work on the modifications in the machine are being carried out.

20.4 *Rubber chemicals*

Sulphides of tetrahydroanacardol have been synthesised and found to possess good antioxidant properties for rubber. The economics of the process is being studied.

Antiozonants based on tetrahydroanacardol possessing urea linkages are also prepared and are being evaluated.

Sulphides of anacardol have been synthesised which are expected to find use as reclaiming agents for rubber. Cashewnut shell liquid is the source used for anacardol and tetrahydroanacardol.

20.5 *Rubber base sealants*

Different metal to metal adhesives and sealants have been prepared and their final evaluation reports are awaited.

P. 21 GRAFTING ON CELLULOSE

Studies have been initiated to improve certain properties such as resistance to microorganisms and mold, and to 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 has been grafted with acrylonitrile using 0.1 N ceric sulfate in 1N nitric acid at 15-25° for 3-4 hours in an inert atmosphere. The homopolymer is removed by shaking the samples with dimethyl formamide at room temperature for about 48 hours. The sample is later washed with methanol. The degree of grafting is determined from the increase in weight over that of the original untreated sample and also by hydrolysing the —CN groups with alkali and estimating resulting —COOH groups volumetrically. 20 hanks of cotton weighing 2 gms. each have been grafted under different conditions of temperature and pH and maximum degree of grafting so far obtained is 15%.

P. 22 PROCESS DEVELOPMENT

22.1 *Vitamin B_6*

A detailed report on the pilot scale work carried out so far has been prepared. Approximate cost estimates have been prepared. The raw material and equipment requirements for a 2000 kg./year plant have been worked out. Negotiations for release of the process are in progress.

22.2 *Vitamin C*

A process essentially based on the Reichstein synthesis, had been worked out on the pilot plant scale. Hindustan Antibiotics Ltd., Pimpri, put up a larger pilot plant to try the same in detail. The process was satisfactorily demonstrated in their unit and a project report of a 125 T/year plant has been prepared by HAL in consultation with our scientists.

Work to improve various steps involved in the synthesis of vitamin C has resulted in encouraging results.

22.3 *Acetanilide*

Acetanilide is an important intermediate used in the preparation of some of the sulfa drugs and coal tar azo colours. The estimated annual requirement of acetanilide for sulfa drugs alone is 2000 T.

Work was taken up in August 1965, and the reaction of acetic acid and aniline was carried out on 20 kg./batch scale. Optimum conditions for a consistent yield of 97% acetanilide of 99.6% purity were obtained. Further, the process was successfully tested on a 60 kg./batch scale in March 1966.

The process details and chemical engineering desings for a 2000 T/year plant have been released to a project engineering firm for supplying a turn-key plant to interested parties.

22.4 *Phthalates* (Dioctyl and Dibutyl)

Dioctyl and dibutyl phthalates are widely used as plasticizers for many types of plastics. The estimated demand of these chemicals is about 10,000 T/year.

Process data for a batch process for the esterification of butyl/octyl alcohol with phthalic anhydride without the use of any azeotropic agent have been obtained, and optimum conditions of temperature, mole ratio and catalyst concentration have been found out. The maximum batch size used for dioctyl phthalate was 70 kg. and for dibutyl phthalate 25 kg.

The processes and plant designs for these two chemicals have been so developed that essentially the same equipment can be used for their commercial manufacture.

Process details and chemical engineering designs for 8500 T/year dioctyl phthalate and 1500 T/year dibutyl phthalate have been released to a project engineering firm, who will undertake plant installation work for private parties interested in the commercial production.

P. 23 PROCESS DESIGNS

Chemical and process engineering designs for the processes developed either on laboratory scale or pilot plant scale, provide the necessary link between the development of a process and its eventual commercial exploitation. Details such as process conditions and energy flow-sheets, equipment specifications and instrumentation diagrams are worked out so as to facilitate complete mechanical design, fabrication and installation of the commercial plant.

Process design work on the following projects has been completed :

(i) Opium alkaloids — 5 T morphine/year

(ii) Dimethylaniline — 600 T/year

(iii) Acetanilide — 2000 T/year

(iv) Phthalates — 10,000 T/year

The designs of aniline and hexachloroethane plants are in progress.

24.1 *Latent heats of vaporization*

A graphical correlation was developed using the acentric factor as a parameter. This correlation was found to be satisfactory when tested for a number of substances, both organic and inorganic including metals. The average and maximum errors are found to be 1·65% and 10.9% respectively.

24.2 *Prandtl number of organic liquids*

Prandtl numbers (Np_r) are important in heat transfer calculations. Lack of reliable data on Cp, μ and K often makes it difficult to calculate this directly. It has to be estimated by other methods in such cases. It was felt that Denbigh's correlation, which relates Prandtl numbers with the heat of vaporization at normal boiling point could be improved with more recent data.

Starting with reliable basic data on twenty organic substances at temperature range —80° to 100°, it was found that the Prandtl numbers of these liquids could be correlated according to the relations

$$\mathrm{Log}_{10}\cdot N_{Pr} = \frac{0{\cdot}04\Delta H_V}{T} - 0{\cdot}22 \qquad \ldots \qquad \ldots \quad (1)$$

$$\text{and} \quad \mathrm{Log}_{10}\cdot N_{P_r} = (\Delta H_V - 7600)\, 2{\cdot}9 \times 10^4\, T^{-3\cdot 2} + 0{\cdot}56 \qquad \ldots \quad (2)$$

Equation (1) holds for non-polar and slightly polar (or nearly non-polar) liquids while equation (2) is considered to be suitable for polar liquids. The accuracy of the predicted values tested with several more compounds, is considered to be satisfactory for engineering purposes.

24.3 *Dependence of fluidized bed characteristics on relative pressure drops in the grid and the bed*

The effect of grid pressure drops in gas and fluidized systems has been studied. Five different solid particles were used and gas velocity L/D was employed as an important variable. The onset of slugging observed by a light flash method, increased with increase in grid resistance till it attained a nearly constant value at each L/D. Optimum grid/bed pressure drop ratios were graphically determined and found to decrease with increase in L/D for all solid particles. Effect of column diameter and grid particles diameter were also noted. The study indicated that the optimum pressure drop ratios recommended by previous investigators do not necessarily hold true as a general rule. On the other hand, these optimum ratios essentially depend on the particle properties, grid geometry and the fluidized-bed geometry. Effect of grid resistance on the bed pressure drop fluctuations, bed level fluctuation and mean bed voidage were also noted.

24.4 *Thermodynamics, kinetics and reactor designs*

This is a continuing research programme with the following principal objectives : Development of methods for the prediction of thermodynamic and transport properties, development of rate models for different types of reactions, and chemical reactor analysis. These studies constitute an integrated effort to extend the theory of engineering kinetics, and to work out new and accurate methods for the estimation of thermodynamic properties. A theoretical understanding of these areas is essential in scale-up and process calculations.

24.4.1 *Thermodynamic and transport properties* : (a) Methods have been developed for estimating liquid density from critical properties using the expansion factor of Watson. (b) Charts have been prepared from theoretical considerations for the estimation of viscosity of any substance over a wide range of temperature and pressure; this analysis takes into account the variation of critical compressibility which has been employed as a correlating parameter. (c) Two methods have been developed for estimating the diffusivity of a substance in a liquid. One of them is an improvement of the Wilke-Chang equation which is commonly used in engineering practice and the other is based on Eyring's diffusion equation. (d) Work is in progress on the development of procedures for the estimation of heat of fusion, entropy of formation, thermal conductivity and liquid heat capacity. Methods have already been developed earlier for ideal heat capacity, heat of formation and latent heat of vaporisation.

24.4.2 *Kinetic models* : Kinetic models have been developed for a variety of reactions involving different systems. During the period under review, the following additional models have been established : (a) an empirical rate equation has been developed for the hydrogenation of anacardol (obtained from cashewnut shell liquid) to tetrahydroanacardol in a vibratory reactor. Tetrahydroanacardol is used in the preparation of heat exchange liquids (ethers). (b) Rate models have been proposed for all the reactions occuring during the dehydration of ethanol over Indian bauxite. Experimental investigations on the determination of rate models for the dehydration of hexanol are nearing completion, and work will be commenced on a series of aliphatic alcohols up to C_{10} using Indian bauxite as catalyst (c) A probable model has been proposed for the vapour phase hydrogenation of o-nitrotoluene to o-toluidine over a catalyst prepared in this laboratory. (d) Work is in progress on the determination of rate models for the oxidation of benzene and toluene. Several competitive models have been developed and on the basis of error analysis the most probable one will be selected. (e) A new MT reactor has been set up and the oxidation of benzene is being studied in this reactor system which is believed to be optimal for reactions of this type. Experimental verification of the optimality criterion is being sought. (f) Theoretical equations have been developed for determining the effect of mixing in a consecutive reaction for system in which the mixed and tubular reactors are used in both the possible sequences.

24.4.3 *Reactor design and fluidization* : (a) Work is in progress on the design of reactors heated by fluidized solids in which the quality of fluidization is improved by the introduction of multi-tubular inserts which serve as reactors. (b) Work on the theoretical and experimental aspects of semi-fluidization is in progress. Equations are being developed for predicting the performance of semi-fluidized beds. 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. (c) A large scale fluidized bed reactor is being set up to study the quality of fluidization as a function of several variables. A novel method is being used as a measure of fluidization quality.

24.5 *Mass transfer*

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.

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

The extensive data available on liquid-liquid extraction have been statistically analysed and a completely general equation has been developed for predicting the onset on 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.

It was found in an earlier investigation that perforated rotors, instead of unperforated rotors as in the conventional R. D. C., could imorove mass transfer. This suggested that sieve rotors may further help to enhance mass transfer. With this view, the effect of sieve plates on flooding velocity and mass transfer is being studied. Data on flooding velocities are being determined in the first instance.

MISCELLANEOUS WORK

25.1 *Foundry chemicals*

In modern foundry practice different types of foundry chemicals are employed, mainly to increase the productivity and to impart high dimensional accuracy, and good surface finish, to moulds and cores.

Active collaboration was rendered to a local paint and varnish manufacturing firm for the large-scale preparation of air hardening foundry core oil. Successful field trials of the product were taken in a few leading foundries. The firm is now engaged in the commercial production of the product.

Sinol type core binders are the compositions generally based on waste sulphite liquor and triethanolamine. These are used in foundry practice where high tensile strength for the core and minimum smoking characteristics in the core after baking are desired. Based on sulphite liquors available from Indian paper mills and the cashewnut shell liquid, a suitable composition has been developed which is found satisfactory in laboratory tests. Preparation of the product (3.5 kg./batch) has been undertaken and samples will be sent to different parties for evaluation.

Dry foundry core binders contain usually dextrinised starch and allied materials. A new type of dry foundry core binder has been developed using waste sulphite liquor as the basic constituent. The product will be cheaper and better than the similar marketed products and has been found to give off much less smoke after baking. Consumer acceptibility trials of the product will be undertaken shortly

25.2 *Television radio suppression ignition cable*

This is a special type of high tension cable with distributed resistance. The problem for the preparation of the distributed resistor core was referred by LRDE, Bangalore. Samples prepared in the laboratory have been found by them to be quite comparable with the imported ones. In near future when use of television sets get popular in India, this type of cable will be required to be fitted in all automobiles.

25.3 *Preparation of catalyst grade nickel formate*

A process for the preparation of catalyst grade nickel formate was worked out in collaboration with RRL, Hyderabad. In all 15 kg. of the catalyst has been prepared for testing and evaluation. Laboratory tests indicate satisfactory results.

25.4 2,4-*Dinitro resorcinol and mono-nitro resorcinol*

Technical preparations of the above chemicals have been standardized on a laboratory scale with improved yields. 10 kg. of the 2,4- dinitro resorcinol has been supplied to a Govt. department on their request.

25.5 *Preparation of biochemicals*

Preparatory conditions for the following biochemicals have been standardized on laboratory scale :
crystalline lysozyme, α – ketoglutaric acid,
oxalacetic acid and γ, γ– dipyridyl.

25.6 *Recovery of mercury*

A chemical method has been worked out for the recovery of mercury from the sludge of caustic chlorine plant. The method is being evaluated.

25.7 *Utilisation of bauxite sludge*

From the bauxite sludge available from aluminium industry, a coloured pigment has been obtained directly. The pigment may find good use in paint industry.

APPENDICES

A-I PROCESSES IN PRODUCTION

1. Anion exchange resin from melamine
2. Antipriming compositions (sponsored)
3. Cation exchange resin from CNSL
4. Can sealing composition
5. Dihydroisojasmone and peach aldehyde
6. Heat sealable coating compositions
7. Hexylresorcinol
8. 4-Hydroxycoumarin
9. β-Ionone
10. Liquid rubber
11. Nicotine sulphate
12. Rigid filters
13. Rubber base adhesive
14. Silica gel (desiccant type) (sponsored)
15. Sisal wax
16. Thermistors
17. Water dispersible DDT

A-II PROCESSES RELEASED AND AWAITING PRODUCTION

1. Acetanilide
2. Acriflavine (sponsored)
3. Ammophos II
4. Bacterial diastase and protease
5. Berberine hydrochloride (sponsored)
6. Chlorinated alkyl aryl phenols as pesticides from CNSL and BNSL
7. Coating compositions for textile bobbins
8. Covering materials from anacardic material
9. Diethyl-m-aminophenol (sponsored)
10. Diethylstilbestrol
11. Ethyl acetoacetate
12. Ethylene dichloride from alcohol and chlorine
13. Foundry core oil
14. Golden yellow GK (sponsored)
15. Hexachloroethane
16. Mixed N. P. fertilisers
17. Opium alkaloids (sponsored)
18. Phthalates
19. Polyurethane printing rollers
20. Pressure sensitive adhesive tapes
21. Reactive dyes (sponsored)
22. Solvent and heat exchange liquids from CNSL
23. Styrene DVB-base cation exchange resin
24. Surface active agents from CNSL
25. Tetrabromoindigo (sponsored)
26. Thiodiglycol (sponsored)
27. Utilisation of byproducts of Hindustan Insecticides Ltd. Delhi (sponsored)
28. Vitamin C

A. III PROCESSES ON WHICH TECHNICAL KNOW-HOW HAS BEEN DEVELOPED (upto March 1965)

(These are under evaluation)

1. Carbon tetrachloride and chloroform from sewage methane
2. Chlorides of barium and strontium
*3. Chromatographic alumina
*4. Chromatographic silica gel
*5. Civetone
*6. Costus root oil
*7. Dihydrocivetone
*8. Dihydrojasmone
*9. Dihydroambrettolide and isoambrettolide
*10. Exaltone and exaltolide,
11. Ferro-electric compositions
12. Gelatine
13. Hard and soft ferrites
14. High alpha-cellulose pulp and vanillin from groundnut shells
15. 4-Hydroxycarbostyrils
16. Low temperature lubricant for clocks and watches
17. Luminescent materials
18. *l*- and *dl*-menthol from citronellal
19. Modified sugarcane wax
20. Neo-lavandulol
*21. Phenoxy-acetic acid
22. Sorbitol
23. Theophylline
24. Titanium incorporated insulating varnish
25. Vanadium catalyst
26. Vitamin B_6

---

* These items are being produced and sold through FCP.

A-IV PROJECTS COMPLETED DURING 1965-66

Sponsored

1. Acriflavine
2. Diethyl-m-aminophenol
3. Golden yellow GK
4. Isolation of berberine hydrochloride from berberis bark
5. Reactive dyes

Pilot plant

1. BON acid
2. Dimethylaniline
3. Titanium tetrachloride from ilmenite (Now sponsored)

Other projects

1. Acetanilide
2. Phthalates
3. Rubberised cork sheets
4. Styrene-DVB anion exchange resins
5. Vapour phase chromatograph (Design of a prototype unit)

A-V SERVICES RENDERED TO OUTSIDE PARTIES

Supply of cultures

634 cultures from NCIM were supplied to various pharmaceutical industries, Govt. departments, research institutes etc.

Analytical services

Microanalysis	..	94 samples
VPC analysis	..	65 „
IR analysis	..	27 „
UV analysis	..	10 „
X-ray diffraction patterns		20 „
Electron diffraction patterns		7 „
NMR spectra	...	26 „

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

6 mercury pulse delay tanks reconditoned for IAF radars, Poona-6.

A Brookfield viscometer repaired for Defence Research & Development Organisation, Poona.

A photometer repaired for Maharashtra Engineering Research Institute, Nasik.

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

Three patients from AFMC, Poona examined for possible thyroid disorder by measuring the uptake of radioactive iodine. Percentage absorption of radioactive cobalt labelled vitamin B_{12} measured in two anaemic patients.

In collaboration with CPHERI, Nagpur, work continued on " H. E. Factory acid waste " with the treatment of ion exchange resin at their field unit near Swargate Water Works, Poona.

A combustion tube of silica, fabricated for Explosive Research & Development Laboratory, Kirkee.

Samples of potatoes, tomatoes and bananas irradiated in Co^{60} radiation source for CFTRI, Mysore.

A sample of cellulose from M/s Cellulose Products, Kathiawar, tested for DEAE-cellulose preparation.

Assistance rendered to Department of Pharmacology, B. J. Medical College, Poona in preparation of test systems for biological assays.

Facilities extended to CSMCRI, Bhavnagar, to irradiate samples of sea-weeds, bittern, brine and ammonium molybdate.

Facilities extended to FRI, Dehra Dun for fluidized bed treatment of wood samples.

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

Costus root oil extracted and processed from 100 kg. costus roots on behalf of M/s Panchi Ram & Co., Manali.

Following glass fabrications have been made :

Dewar flasks, Glass coil and Vessel as per design	Institute of Armament Technology, Kirkee.
Ground glass joints	Maharashtra Association of Cultivation of Science, Poona.

A-VI DEMONSTRATIONS

1. Acetanilide	M/s R. L. Dalal & Co., Bombay.
2. Acid resistant covering materials from CNSL	M/s Natson Mfg. Co., Ahmedabad.
3. Ethyl acetoacetate	M/s Indian Organic Chemicals, Ltd., Khopoli.
4. Extraction of opium alkaloids. (few steps)	Technological Consultancy Bureau, New Delhi.
5. Phthalates	M/s R. L. Dalal & Co. Bombay.
6. Polyurethane printing rollers	M/s Saraswati Press, Calcutta. M/s United Ink & Varnish Co., Bombay.
7. Reduction of menthone to menthol (sponsored work in progress)	M/s Bhavana Chemicals, Baroda.
8. Test runs of vapour phase chromatograph	M/s Associated Instrument Manufacturers, Bombay. M/s Blue Star Engg. Co., Bombay.
9. Vitamin C	M/s Hindustan Anti-Biotics Ltd., Pimpri.

A-VII TRAINING

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

Glass blowing, Spectroscopy, Microbiological techniques, Chromatographic techniques, Microanalysis, etc.

A-VIII TECHNICAL SERVICES

Feasibility reports prepared on the following projects :

Parathion, Malathion, Ethanolamines, Ethylamines, Methylamines, Ethyl chloride, Ethylene diamine, Glycol ethers, Sevin, α-Naphthol and Methyl isocyanate.

Evaluation reports prepared on the following NCL projects :

Neo-lavandulol, Iso-ambrettolide and Styrene–DVB anion exchange resin.

PERT (Project Evaluation Review Technique) applied to the following projects :

Dioctyl phthalate, Dibutyl phthalate and Sorbitol.

Market survey on vapour phase chromatograph done to estimate its tentative demand in the country.

A-IX SPECIAL FABRICATIONS

A dual column vapour phase chromatograph with a thermal conductivity detector and facility for temperature programming 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 fabricated. Measurements indicate that it is capable of detecting 10^{13} spins $\triangle$ H which is sufficient for carrying out a majority of the measurements in ESR.

Eleven exhaust blowers.

A stainless steel paint grinding pot.

A stainless steel ball mill.

One opium extraction unit.

A stainless steel bleacher.

Three thin layer applicators.

A-X SEMINARS AND LECTURES

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

Prof. O. M. Poltorak, Visiting Professor, USSR.	Kinetics of heterogeneous catalytic reactions Heat disorder in real crystals and activated centres of catalyst. Electronic theories of catalysis on semiconductors.
Dr. H. R. C. Pratt, CSIRO, Australia.	Process development and chemical engineering research in CSIRO, Australia.
Dr. H. M. McNair, Wilkins Instrument research Inc., U. S. A.	Preparative scales gas chromatography.
Prof. R. C. Brasted, University of Minnesota, U. S. A.	Optical rotary dispersion of complex compounds.
Prof. R. D. DeMoss, University of Minnesota, U. S. A.	Metabolism of tryptophane.
Dr. P. A. Ongley, College of Advance Technology, Birmingham, U. K.	Chemistry of benzcyclobutene.
Dr. Cohn, Salk Institute for Biological Studies, San Riego, California, U. S. A.	Structure of antibodies.
Dr. Mrs. Cohn, California, U.S.A.	Nature of the repressor.
Prof. J. H. Quastel, FRS, University of Montriel, Canada.	Molecular transport at cell membranes.
Prof. G. Fodar, University of Lavel, Canada.	Recent advances in the chemistry and stereochemistry of tropane alkaloids.
Dr. O. N. Talkachev, Russian scientist.	Investigations in the field of alkaloids and lipids.

Dr. Grenevitch, Russian scientist.	Some questions of pocked twines with suggested pocklings.
Dr. A. K. Mitra, Jadavpur University, Calcutta.	Exceptional unhydro sugar formation.
Dr. J. V. Naralikar, University of Cambridge, U. K.	The origin of elements.

25 NCL scientists delivered more than 30 scientific lectures on different subjects at various research institutes and universities, in the country.

A. XI SYMPOSIA

A symposia on ‘Recent Advances in the Chemistry of Terpenoids’. organised by the National Institute of Sciences of India and Kurukshetra University, was held in the NCL from 7th to 10th June 1965. 10 foreign scientists, and 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.

A. XII STAFF NEWS

Foreign deputations/training etc.

On the invitation of the West German Academic Exchange Service, Prof. K. Venkataraman visited West Germany for a period of 3 weeks in June 1965.

Shri S. P. Mukherjee proceeded to France under Indo-French agreement from June 1965, for training in the field of chemical engineering.

Dr. S. C. Bhattacharyya visited USSR for 4 weeks in July 1965 under Indo-Soviet Cultural Programme. He delivered lectures at various universities and research institutes in the USSR.

Dr. C. G. Joshi worked in Geneva for 6 months from Aug. 1965 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, in Aug. 1965 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) organosilicones held at Prague At the invitation of the University of Mainz, West Germany, he visited few polymer industries and delivered lectures at various polymer research centres in West Germany (Aug. 1965).

Shri N. V. Viswanathan proceeded to Japan in Nov. 1965 under Japanese National Commission, UNESCO and the Tokyo Institute of Technology to participate in International postgraduate university course in chemistry and chemical engineering.

Shri P. S. Kulkarni proceeded to Australia in Jan. 1966 for training in the field of mass spectrometric techniques, under Colombo Plan's Technical Assistance Services of Foreign Experts.

Awards and Honours

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.

Degrees received by NCL staff (1965-66)

Mr. Bhat, N. A.	M. Sc.	Bombay
Mr. Bisarya, S. C.	Ph. D.	Agra
Mr. Chetty, G. L.	Ph. D.	Agra
Mr. Damodaran, N. P.	Ph. D.	Poona
Mr. Deo, V. D.	M. Sc. (Tech)	Bombay
Mr. Dhekne, V. V.	Ph. D.	Bombay
Mr. Gupta, R. K.	Ph. D.	Agra
Mr. Gupta, S. S.	Ph. D.	Bombay
Mr. Iyer, K. N.	Ph. D.	Bombay
Mr. Jagtap, S. S.	M. Sc. (Tech)	Bombay

Mr. Jain, S. K.	Ph. D.	Bombay
Mrs. Joglekar, P. P.	Ph. D.	Poona
Mrs. Jose, Parimala	Ph. D.	Poona
Mr. Joseph, T. C.	Ph. D.	Poona
Mr. Kantak, U. R.	M. Sc.	Poona
Mr. Kartha, C. C.	Ph. D.	Poona
Mr. Keer, H. V.	M. Sc.	Bombay
Mr. Kulkarni, K. S.	Ph. D.	Poona
Mr. Lobo, J.	M. Sc.	Poona
Mr. Mascarenhas, A. F.	M. Sc.	Poona
Miss. Misra, R.	Ph. D.	Agra
Mr. Nagasampagi, B. A.	Ph. D.	Poona
Mr. Narayanan, C. S.	Ph. D.	Poona
Mr. Pethe, L. D.	Ph. D.	Bombay
Mr. Rajan, E. V.	Ph. D.	Poona
Mr. Ranade, A. C.	M. Sc.	Bombay
Mr. Santhanakrishnan, T. S.	Ph. D.	Madras
Mr. Sathe, V. M.	M. Sc.	Poona
Miss. Sayagavar, B. M.	M. Sc.	Bombay
Mr. Upadhyaya, U. N.	Ph. D.	Poona
Mr. Wagh, A. D.	Ph. D.	Poona

NCL Scientists Recognised by different universities, as research guides

Dr. Bhattacharyya, S. C.	Poona, Bombay, Calcutta, Agra, Vikram, Banaras.
Dr. Biswas, A. B.	Poona, Bombay, Punjab, Andhra, Culcutta, Karnatak, Banaras.
Dr. Bose, J. L.	Bombay, Poona, Nagpur.
Dr. Chakravarti, K. K.	Bombay, Poona.
Dr. Dadape, V. V.	Bombay, Poona, Karnatak, Vikram.
Dr. Doraiswamy, L. K.	Poona, Bombay, Nagpur, Banaras’ Calcutta, Jadavpur.

Dr. Dutta, N. L.	Poona.
Dr. Ghatge, N. D.	Poona, Shivaji.
Dr. Goswami, A.	Poona, Calcutta, Punjab.
Dr. Gupta, J.	Poona, Bombay, Punjab, Madras.
Dr. Jagannathan, V.	Bombay, Poona.
Dr. Kapur, S. L.	Poona, Bombay, Punjab.
Dr. Kelkar, G. R.	Poona.
Dr. Kulkarni (Miss), S. B.	Poona.
Dr. Kulkarni, S. N.	Poona, Bombay, Karnatak.
Dr. Mathur, H. B.	Poona, Agra, Madras.
Dr. Narayanan, C. R.	Poona, Bombay.
Dr. Nair, P. M.	Poona.
Dr. Pai, M. U.	Bombay.
Dr. Pant, L. M.	Poona.
Dr. Rao, A. S.	Poona, Bombay.
Dr. Rao, M. R. R.	Bombay, Poona.
Dr. Sadana, J. C.	Poona.
Dr. Sen, D. N.	Poona, Bombay.
Dr. Sinha, A. P. B.	Poona, Banaras, Vikram.
Dr. Sinha, K. P.	Poona, Agra.
Dr. Sivaraman, C.	Poona.
Dr. Subbaraman, P. R.	Poona, Bombay, Gujarat.
Dr. Sukh Dev	Poona, Bombay, Agra, Punjab, I. I. Sc. Bangalore.
Dr. Tilak, B. D.	Bombay, Poona.
Dr. Venkataraman, K.	Poona, Bombay, Madras, Banaras.

A. XIII PUBLICATIONS

Research Papers

1. Jose (Mrs.), Parimala and Pant, L. M. The crystal and molecular structure of β–alanine. *Acta Cryst.* **18**, 806 (1965).

2. Joshi, A. W. and Sinha, K. P. Phonon-magnon relaxation processes in ferrimagnetic systems. *Proceedings of physical Society* (*London*). (Supplement for 1964 magnetism conference), 411 (1965).

3. Biswas, A. B., Deo, A. V., Gharpurey, M. K. and Kulkarni (Miss), S. 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.* **3**, 200 (1965).

4. Narasimhan, K. S.V. L. and Sinha, K. P. Spin effects in bismuth telluride doped with magnetic impurities. *Ind. J. Pure. & Appl. Phys.* **3**, 221 (1965).

5. Kulkarni, P. S., Mathur, H. B. and Sharma, V. S. Stability of transition metal complexes of amino acids. *Ind. J. Chem.* 3, 146 (1965).

6. Badachhape, R. B., Biswas, A. B. and Gharpurey, M. K. Density and surface tension of phenol (mono–, di–and tri–) chlorophenols, salol and (o–and m–) chloronitrobenzenes. *J. Chem. Eng. Data* **10**, 143 (1965).

7. Rao, R. V. G. Phenomenological theory of surface tension and compressibility : Evaluation of the parameter. *Ind. J. Pure & Appl. Phys.* **3**, 233 (1965).

8. Goswami, A. Oxidation of metals in air and reduced pressures. *Ind. J. Chem.* 3, 385 (1965).

9. Pant, L. M. and Sakore, T D. Preliminary structure analysis of p–nitrobenzoic acid. *Ind. J. Pure & Appl. Phys.* 3, 143 (1965).

10. Biswas, A. B., Rao, R. V. G. and Subba Rao, V. V. Thermogravimetric analysis of La, Ce, Pr and Nd oxalates in air and carbon dioxide atmosphere. *J. Inorg. Nucl. Chem.* **31**, 2525 (1965).

11. Gharpurey, M. K. and Rao, R. V. G. Vibrational frequency spectrum of two-dimensional simple square lattice with non-central nearest neighbour forces. *Ind. J. Pure & Appl. Phys.* **3**, 317 (1965).

12. Shukla, G. C. and Sinha, K. P. Collective oscillations in a system of ordered dipoles. *Ind. J. Pure & Appl. Phys.* **3**, 430 (1965).

13. Krishnamurthy, B. S. and Sinha, K. P. Theory of carrier mobility in polar semiconductors. *J. Phys. Chem. Solids* **26**, 1949 (1965).

14. Chandra (Mrs.), Saraswati and Roy Chowdhury, P. Ultrasonic degration of butyl rubber in solution. *Ind. J. Chem.* **3**, 338 (1965).

15. Subba Rao, V. V. Calcination and sintering study of ceria. *Ind. J. Chem.* **3**, 343 (1965).

16. Biswas, A. B., Mathur, H. B. and Sharma, V. S. Order of stability and the shift in the N-H stretching frequency in metal-amino acid complexes. *Britt. National Institute Sciences, Bulletin* **29**, 153 (1965).

17. Mathur, H. B., Sharma, V. S. Thermodynamic properties of coordination complexes of transition metal ions with aminoacids. *Ind. J. Chem.* **3**, 475 (1966).

18. Mathur, H. B., Sinha, A. P. B. and Yagnik, C. M. Mössbauer spectra of spinel oxides containing ferrite ion. *Solid State Comm.* **3**, 401 (1966).

19. Borcar, M. D. S. (from AFMC), Kippr Swamy, G., Malhotra, O. P., Mathur, H. B., Matrias, P. F. and Nayak, K. K. A study of thirtytwo Indian cases of magaloblastic anaemia. *J. Tropical Medicine and Hygiene U. K.* **68**, 147 (1966).

20. Biswas, A. B., Rao, R. V. G. and Subba Rao, V. V. Calcination of lanthanum and praseodymium oxalates and changes in surface area of the products. *Ind. J. Chem.* **3**, 482 (1965).

21. Pant, L. M. Diffuse X-ray scattering from neutron-irradiated graphite. *Acta Cryst.* **20**, 354 (1966).

22. Badachhape, R. B., Gharpurey, M. K., Katti, S. S., Kulkarni (Miss), S. B. and Shukla, R. N. Micronization of DDT by spray crystallization of supercooled melt. *Ind. J. Technol.* 4, 18 (1966).

23. Ganguly, B. N. and Sinha, K. P. Pressure effects on the transition temperature of super-conductors. *Ind. J. Pure & Appl. Phys.* **4**, 49 (1966).

24. Krishnamurthy, B. S. and Sinha, K. P. Theory of carrier mobility in polar semiconductors–II. Solid solutions. *J. Phys. Chem. Solids* **27**, 629 (1966).

25. Kumar, N. and Sinha, K. P. A generalised direct exchange interaction – application to Heusler alloys. *Ind. J. Phys.* **4**, 62 (1966).

26. Navangul, H. V. Electron gas model of mobile electrons in some complex conjugated system. *Ind. J. Chem.* **4**, 101 (1966).

27. Nageswara Rao, B. B. S., Rao, P. S. and Reddy, M. P. Spectrophotometric determination of α and β- naphthols in a mixture. *Ind. J. Chem.* **3**, 408 (1966).

28. Sen, D. N. and Thankarajan, N. Aluminium nitrate and nitric acid as nitrating agents for acetylacetonates. *Ind. J. Chem.* **3**, 215 (1965).

29. Gopinathan, C. and Gupta, J. Organoxy-titanium compounds. *Ind. J. Chem.* **3**, 231 (1965).

30. Homawala (Miss), T. K., Shetty, P. S. and Subbaraman, P. R. Iodometric estimation of gold. *Ind. J. Chem.* **3**, 348 (1965).

31. Dadape, V. V. and Kuruvilla Joseph. Studies in the chlorination of Indian bauxite ores. *Ind. J. Technol.* **3**, 244 (1965).

32. Gupta, J., Kundra, S. K., Shah, S. A. and Subbaraman, P. R. Anion exchange fractionation of light lanthanons. *Ind. J. Chem.* **3**, 108 (1965).

33. Hundekar, A. M., Sen, D. N., Srinivasan, K. S. and Thankarajan, N. Potable water from sea-water using briquetted silver barium zeolite. *Indian J. Appl. Chem.* **28**, 203 (1965).

34. Gopinathan, C. and Gupta, J. Ammonia adducts of organoxy-titanium (IV) compounds. *Ind. J. Chem.* **3**, 470 (1966).

35. Apte, B. G., Gupta, J. and Subbaraman, P. R. Ion exchange behaviour of uranium (VI) in aqueous sodium triphosphate and its separation from rare earths. *Ind. J. Chem.* **3**, 454 (1966).

36. Chatterjee, A. K., Gupta, J. and Mukherjee, R. N. *Bis*-(diphenyl dithiophosphinates)-titaniumdichloride. *Ind. J. Chem.* **3**, 514 (1966).

37. Ramaswamy, K. K. and Sen, D. N. Reactivity of chelated salicylaldoxime and a new form of *Bis*-(salicylaldoximato)-copper (II). *Ind. J. Chem.* 3, 516 (1966).

38. Ramaswamy, K. K. and Sen, D. N. Colour isomers of *bis*-(salicylaldoximato) - copper (II). *Ind. J. Chem.* 3, 516 (1966).

39. Sen, D. N. and Srinivasan, K. S. Preparation of spectroscopically pure oxides of cobalt, nickel and manganese for use in semiconductor materials. *Ind. J. Technol.* 4, 23 (1966).

40. Sen, D. N. and Thankarajan, N. Reactivity of chelated Acetylacetone. *Ind. J. Chem.* 4, 94 (1966).

41. Shetty, P. S. and Subbaraman, P. R. Reduction of solid suspensions of vat dyes at the dropping mercury electrode. *Ind. J. Chem.* 4, 90 (1966).

42. Damodaran, V., Gupta, J. and Neurgaonkar, V. G. Rutile titanium dioxide pigment by hydrolysis of titanium tetrachloride. *Ind. J. Technol.* 4, 64 (1966).

43. Joshi, B. S., Ramanathan, S. and Venkataraman, K. Endocrocin. *Bulletin of the National Institute of Sciences of India*, No. 28, 122 (1965).

44. Bhide, N. S., Joshi, B. S., Patwardhan, A. V., Srinivasan, R. and Venkataraman, K. Lac pigments. *Bulletin of the National Institutie of Sciences of India*, *No.* 28, 114 (1965).

45. 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). 607

46. Kapadi, A. H. and Sukh Dev. Chemical transformation of (+)-hibaene into (—) - kaurene. *Tetrahedron Letters* No. 18, 1225 (1965).

47. Radhakrishnan, P. V., Rama Rao, A. V. and Venkataraman, K. Two hawones from *Artocarpus heterophyllus*. *Tetrahedron Letters* No. 11, 663 (1965).

48. 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, 123 (1965).

49. Bose, J. L. and Modi, B. D. Simple spot test for vanillin and some other carbonyl and chelated hydroxy compounds. *Ind. J. Chem.* **3**, 236 (1965).

50. Naik, V. G., Sonawane, H. R. and Subba Rao, B. C. Boron fluoride catalysed alkylations of phenol – Part I. Alkylation with isomeric octanols, octenes and octyl bromides. *Ind. J. Chem.* **3**, 260 (1965).

51 Kapadi, A. H., Sobti, R. R. and Sukh Dev. The diterpenoids of *Erythroxylon monogynum*–V. Atisirene, isoatisirene and devadarene. *Tetrahedron Letters* No. **31**, 2729 (1965).

52. Kaul, B. L., Srinivasan, R. and Venkataraman, K. Structures of azoic coupling compounds and azoic dyes. *Chemia* **19**, 213 (1965).

53. Damodaran, N. P. and Sukh Dev. Strercochemistry of zerumbone. *Tetrahedron Letters* No. **24**, 1977 (1965).

54. Iyer, K. N. and Narayanan, C. R. Mode of cleavage of steroid methyl ether with BF_3 –Etherate. *Tetrahedron Letters* No. **19**, 1369 (1965).

55. Chetty, G. L. and Sukh Dev. Mayurone, a C_{14}–sesquiterpene ketone. *Tetrahedron Letters* No. **42**, 3773 (1965).

56. Iyer, K. N. and Narayanan, C. R. Regeneration of steroid alcohols from their methyl ethers. *J. Org. Chem.* **30**, 1735 (1965).

57. Dutta, N. L. and Ghosh, A. C. Chemical investigation of *Ongeinia dalbergioides Benth. J. Ind. Chem. Soc.* **42**, 381 (1965).

58. Narayanan, C. R. and Venkatasubramanian, U. K. Stereochemical studies by NMR spectroscopy–axial and equitorial acids. *Tetrahedron Letters* No. **41**, 3639 (1965).

59. Linde, H. and Narayanan, C. R. Stereochemistry of salvin and picrosalvin. *Tetrahedron Letters* No. **41**, 3647 (1965).

60. Iyer, K. N. and Narayanan, C. R. An alternate method to identify proton (s) on the carbon bearing a hydroxyl group. *Tetrahedron Letters* No. **42**, 3741 (1965).

61. Narayanan, C. R. and Pachapurkar, R. V. Ring D in nimbin. *Tetrahedron Letters* No. **48**, 4333 (1965).

62. Bhat, V. V. and Bose, J. L. 4-(O-hydroxyphenyl)- cinnolines. *Chem & Ind.* 1955 (1965).

63. Iyer, K. N. and Narayanan, C. R. The conformation of Westphalen's diol diacetate. *Tetrahedron Letters* No. **3**, 285 (1966).

64. Narayanan, C. R. and Pachapurkar, R. V. The structure of nimbinic acid. *Tetrahedron Letters* No. **6**, 553 (1966).

65. Karanjgaonkar, S., Nair, P. M. and Venkataraman, K. Morellic, ismorellic and gambogic acid. *Tetrahedron Letters* No.7, 687 (1966).

66. Bose, J. L. and Patil, J. R. Cyclic acetals and ketals of mono-saccharides – Part I. Isopropylidene sorboses. *J. Ind. Chem. Soc.* **43**, 161 (1966).

67. Bhattacharyya, S. C. , Kulkarni, S. N., Narayanan, C. S., and Welankiwar, S. S. Synthesis of *cis*-norbergamotinic acid. *Tetrahedron Letters* No. **15**, 985 (1965).

68. Bhattacharyya, S. C., Chakravarti, K. K., Ghatge, B. B., Kamat, S. Y., and Ranibai (Miss), P. Terpenoids–LXV. Transformation in the santalene longifolene series. *Tetrahedron* **21**, 629 (1965).

69. Bhattacharyya, S. C., Ghatge, B. B. and Mehra, M. M. Terpenoids–LXVI. Ring enlargement produced by the alkaline fusion of ω–bromo-longifolene. *Tetrahedron* **21**, 637 (1965).

70. Kulkarni, K. S. and Rao, A. S. Terpenoids–LXVII. Synthesis of a ketodicarboxylic acid related to elemol and epidihydroeudesmol. *Tetrahedron* 21, 1167 (1965).

71. Bapat, B. V., Bhattacharyya, S. C. and Ghatge, B. B. Terpenoids–LXIV. Evaluation of polyesters as stationary phases in gas-liquid chromatography of terpenoids. *J. Chromatography* **18**, 308 (1965).

72. Chakravarti, K. K. Stereochemistry of Khusilal. *Ind. J. Chem.* **3**, 324 (1965).

73. Chakravarti, K. K. Stereochemistry of the derivatives of Khusinol. *Ind. J. Chem.* 3, 325 (1965).

74. Bhattacharyya, S. C. , Chakravarti, K. K. and Nayak, U. G. Macrocyclic musk compounds – Part VII. New synthesis of civetone dicarboxylic acid and its conversion to *trans*-civetone. *J. Chem. Soc.* 3475 (1965).

75. Bhattacharyya, S. C. and Mathur, H. H. Macrocyclic musk compounds. Part–IX. New synthesis of cyclohexadecanone. *Tetrahedron* **21**, 1537 (1965).

76. 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).

77. Honwad, V. K. and Rao, A. S. Terpenoids–LXIX. Absolute configuration of (—) α–curcumene. *Tetrahedron* **21**, 2893 (1965).

78. Honwad, V. K. and Rao, A. S. Terpenoids–LXXII. Synthesis of (±) α–curcumene and related compounds. *Current Science* **18**, 534 (1965).

79. Rao, A. S. Terpenoids–LXXIV. A synthesis of (±) curcumene. *Ind. J. Chem.* **3**, 419 (1965).

80. Bhattacharyya, S. C., Chakravarti, K. K., Kalsi, P. S. and Nerali, S. B. Structure of iso-patchoulenone; a new sesquiterpene ketone from the oil of *cyperus scariosus*. *Tetrahedron Letters* No. **45**, 4053 (1965).

81. Bhattacharyya, S. C., Hiremath, S. V., Kelkar, G. R., Kulkarni, G. H. and Mathur, S. B. Structure of dehydrocostus lactone. *Tetrahedron* **21**, 3575 (1965).

82. Bhattacharyya, S. C., Maheshwari, M. L., Meista, C. K., and Shanbag, S. N. Constituents of *Nardostachys jatamansi* and synthesis of dihydrosamidin and visnadin from jatamansin. *Tetrahedron* **21**, 3591 (1965).

83. Bhattacharyya, S. C., Hinge, V. K., Paknikar, S. K. and Wagh, A. D. Constituents of Indian black dammar resin. *Tetrahedron* **21**, 3197 (1965).

84. Chakravarti, K. K., Gore, K. G., and Umrani D. C. Khusimol, a new sesquiterpenic alcohol. *Tetrahedron Letters* No. **12**, 1255 (1966).

85. Bawdekar, A, S., Bhattacharyya, S. C. and Kelkar, G. R. Absolute configuration of parthenolide. *Tetrahedron Letters* No. **11**, 1225 (1966).

86. Bhattacharyya, S. C., Mathur, H. H. and Patnekar S. G. Alkyl cyclopentanones. *Ind. J. Chem.* **4**, 67 (1966).

87. Bhattacharyya, S. C., Maheshwari, M. L. and Shastry, S. D. Structure of nardol. *Tetrahedron Letters No.* **10**, 1035 (1965).

88. Bhattacharyya, S. C., Ghatge, B. B. and Ranibai (Miss), P. Synthesis of iso-bicycloekasantalic acid and related products. *Tetrahedron* **22**, 907 (1966).

89. Honwad, V. K., Rao, A. S. and Siscovic (Mrs.), E. Synthesis of 1-oxo-eudesmanes. *Tetrahedron Letters* No. **14**, 1471 (1966).

90. Chatterjee, A., Kundu, S. K. and Rao, A. S. Isolation of fernenol, a new triterpenic alcohol from *Artemesia vulgaris*. *Tetrahedron Letters* No. **10**, 1043 (1966).

91. Rittenberg, D. and Sadana, J. C. Iron requirement for the hydrogenase of desulfovibrio desulfuricans. *Archive. Biochem. Biophys.* **108**, 255 (1965).

92. Bhattacharyya, P. K. and Dhawalikar, R. S. Microbiological transformations of terpenes–V. The origin of 2–nonene–2, 3-dicarboxylic acid anhydride. *Ind. J. Biochem.* **2**, 73 (1965).

93. Bhattacharyya, P. K. and Ganapathy, K.Microbiological transformations of terpenes, —VI. Studies on the mechanism of some fungal hydroxylation reductions with the aid of model systems. *Ind. J. Biochem.* **2**, 137 (1965).

94. Altekar (Mrs.), W. W., Bhattacharyya, P. K., Maskati (Miss), F. S. and Rao, M. R. R. Aconitate isomerase in sugarcane. *Ind. J. Biochem.* **12**, 132 (1965).

95. Jagannathan, V., Mascarenhas. A. F. and Sayagaver (Miss), B. M. Studies on the growth of callus cultures of *Zea mays*. *Tissue culture* 283 (1965).

96. Sadana, J. C. Purification and characterization of nitrite reductase from *A. fisheri*. *Proc. Soc. Biol. Chemists, India* **24**, 12 (1965).

97. Sadana, J. C. Purification and characterization of nitrite reductase from *Achromobacter fisheri*. *Biochim. Biophys. Acta.* **118**, 426 (1966).

98. Jagannathan, V. and Kaplay, S. S. Purification of ox brain acetylcholinesterase. *Ind. J. Biochem.* **3**, 54 (1966).

99. Rao, M. R. R. and Subramanian S. S. Enzymatic preparation of (—) and (+) isomers of citramalic acid. *Ind. J. Biochem.* **3**, 19 (1966).

100. Ghatge, N. D. and Gokhale, R. G. Development of rubber chemicals on small scale in India. *Rubber News* **7**, 28 (1965).

101. Krishnaswamy, N. Ion exchange membranes–Synthesis and applications. *J. Sci. Industr. Res.* **24**, 244 (1965).

102. Dasare, B. D. and Krishnaswamy, N. Studies on anion exchange resins–II. Preparation and properties of an anion exchange based on cashewnut shell liquid and tetraethylene pentamine. *Ind. J. Technol.* **3**, 212 (1965).

103. Deshpande, A. B., Kapur, S. L. and Subramanian, V. An improved stirrer assembly for use in thermostats. *Ind. J. Chem.* **3**, 426 (1965).

104. Narsimhan, G. A generalized expression for predicting latent heat of vaporization of liquids. *Brit. Chem. Eng.* **10**, 4 (1965).

105. Deshpande, A. D., Pai, M. U. and Thangappan Nadar, Fluidization of mixed materials. *Ind. J. Technol.* **3**, 111 (1965).

106. Pai, M. U. and Rao, M. K. Ternary liquid equilibria of butyric acid-water-ethyl acetate/butyl acetate systems. *Ind. J. Technol.* **3**, 178 (1965).

107. Narsimhan, G. A generalized chart for saturated liquid densities. *Ind. J. Technol.* **3**, 230 (1965).

108. Doraiswamy , L. K. and Phadtare, P. G. Mass transfer model for Kolbeschmitt carbonation of 2-naphthol. *J. I. & EC. Process Design and Development* **4**, 274 (1965).

109. Babu Rao, K.. Doraiswamy, L. K. and Mukherjee, S. P. A new adiabatic MT reactor system. *A. I. Ch. E. J.* **11**, 741 (1965).

110. Krishnaiah, M. M., Pài, M. U. and Sastri, S. R. S. Enthalpy concentration diagram for the system, carbon tetrachloride–chloroform. *J. Chem. Eng. Data* **10**, 117 (1965).

111. Krishnadas, M. S. and Pai, M. U. Equilibria in the oxalic acid-tartaric acid-water system. *J. Chem Eng. Data* **10**, 97 (1965).

112. Pai, M. U. and Sastri, S. R. S. Correlation of latent heats of vaporisation. *Ind. J. Technol.* 4, 72 (1966).

113. Doraiswamy, L. K., Narayanan, T. K. and Rihani, D. N. Kinetics of catalytic vapour phase hydrogenation of nitrobenzene to aniline. *I. & EC. Process Design & Development* 4, 403 (1965).

114. Doraiswamy, L. K. and Varma, K. K. Estimation of heats of formation of organic compounds. *I. & EC.* 4, 389 (1965)

Papers sent/read at symposia, seminar etc.

115. Goswami, A. and Koli, S. S. Semiconducting properties of PbTe films. International symposium on basic problems in thin film physics, W. Germany, Sept. 1965.

116. Devkar, V. D. and Goswami, A. Some studies on Hall effects on thin films. International symposium on basic problems in thin film physics, W. Germany, Sept. 1965.

117. Badachhape, S.B. and Goswami, A. Epitaxial growth of cuprous halides on single crystal substrates. International symposium on basic problems in thin film physics, W. Germany, Sept. 1965.

118. Goswami, A. Epitaxial growth and crystal structure. International conference on electron diffraction and nature of defects in crystals, Australia, Aug. 1965.

119. Fairwell, T., Gopakumar, G. and Nair, P. M. Long range spin-spin coupling in the study of aromatic π-electrons. International symposium on nuclear magnetic resonance, Tokyo, Sept. 1965.

120. Jagannathan, V. and Joshi (Miss), M. D. Brain hexokinase. Symposium on regulatory mechanism, New Delhi, Dec. 1965.

121. Subramanian, S. K. Organising research for industry. Get- To-gether of Research & Industry, New Delhi, Dec. 1965.

122. Mathur, H. B. and Yagnik, C. M. Mössbauer effect as a tool in the the study of cation distribution in cubic ferrites with spinel structure. Symposia on nuclear and solid state physics, Bombay, Feb. 1966.

123. Kapur, S. L. (1) A new fibre for tyre cord. (2) Preparation and properties of modified rubber. IRMRA seminar, Calcutta, Feb. 1966.

124. Narayanan, C. R. A new method to identify protons, on carbon bearing a hydroxyl group. 53rd Indian Science Congress, Chandigarh, Jan. 1966.

125. Pant, L. M. The structure of p-nitrobenzoic acid. Symposia on crystallography, Madras, Feb. 1966.

126. Goswami, A. Studies on semiconducting properties of thin films. Seminar on physics in and around Poona, Poona, March 1966.

127. Ghatge, B. B. Application of gas liquid chromatography in essential oils. Annual convention of Essential Oils Association of India, Bombay, March 1966.

128. Sadana, J. C. Purification and properties of nitrite reductase from *A. fischeri*. Symposia on regulatory mechanism, New Delhi, Dec. 1965.

129. Roy Choudhury, P. Design and construction of an ultrasonic interferometer. Seminar on electronic instrumentation, Jan. 1966.

130. Ghatge, N. D. Polysulphide rubbers and their production in India. IRMRA seminar, Calcutta, Feb. 1966.

131. Doraiswamy, L. K. Ethylene dichloride-a process development study through model building. Symposium on process design, Bombay Jan. 1966.

General Science Papers :

132. Ghatge, N. D. and Phadke, V. B. Recent developments in polyurethane elastomers. *Rubber News* **2**, 22 (1965).

133. Seth, N. D. and Subramanian, S. K. Weeds : A burden on our crops. *Chemical Age of India* **16**, 764 (1965)

134. Lele, A. M. and Subramanian, S. K. NCL's contribution to industry. *Economic Times* 30th June 1965.

135. Adke (Mrs.), S. S., Natarajan, E. S. and Subramanian. S. K. Guestimating chemical manufacturing costs. *Economic Times* 21st March 1965.

136. Adke (Mrs.) S. S., Kelkar, D. D. and Subramanian S. K. Capital costs of AC motors. *Chemical Age of India* **16**, 941 (1965).

137. Adke (Mrs.), S. S., Kelkar, D. D. and Subramanian, S. K. Simplified technique for estimating centrifugal pump costs. *Chemical Age of India* **16**, 855 (1965).

138. Subramanian, S. K. Forecasting in the chemical industry. *The Materials Management Journal of India* **6**, 201 (1965).

139. Deshpande, A. B. and Kapur, S. L. A new fibre for tyre cord. *Silk & Rayon* **3**, 95 (1966).

140. Kapur, S. L. and Srinivasan, S. R. Plastic butt ends. *R & D Digest* (Ministry of Defence) **5**, 110 (1965).

141. Kapur S. L. Plastics. *Science Reporter* **10**, 429 (1965).

142. Kapur, S. L. Recent trends in research in plastics. *Souvenir, Gujarat Small Industries Association, Ahmedabad,* Feb. 1966.

Reviews.

1. METHODS IN MICROANALYSIS, Vol. 1, SIMULTANEOUS RAPID COMBUSTION. (By J. A. Kuch; Gordon & Breach Science Publishers N. Y. 1964) Pansare V. S. *J. Sc. Industr. Res.* **24**, 381 (1965)

2. 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) Biswas, A. B. *J. Sc. Industr. Res.* **24**, 252 (1965).

3. FERROMAGNETIC RELAXATION THEORY. (By M. Sparks, McGraw-Hill Book Co., 1964) Sinha, K. P. *J. Sc. Industr. Res.* **24**, 644, (1965).

4. ELECTRONIC CHANGES OF BONDS IN ORGANIC COMPOUNDS. (By G. V. Bykore, translated from Russian by J. T. Greaves, edited by R. W. Clarke, Pergamon Press Ltd., Oxford, 1964) Nair, P. M. *J. Sc. Industr. Res.* **24**, 314 (1965).

5. ANALYSIS OF ANCIENT METALS, Vol. 19, INSTRUMENTAL SERIES OF MONOGRAPHY ON ANALYTICAL CHEMISTRY. (By E. R. Caley, Pergamon Press Ltd., Oxford, 1964) Gupta, J. *J. Sc. Industr. Res.* **24**, 252 (1965).

6. HIGH POLYMERS, Vol. XIII. (Edited by N. G. Gaylord, Interscience Publishers, Inc., New York, 1963) Kapur, S. L. *J. Sc. Industr. Res.* 24, 253 (1965).

7. BIOCHEMISTRY OF PHENOLIC COMPOUNDS. (By J. B. Harborne, Academic Press Inc. London, 1964) Venkataraman, K. *J. Sc. Industr. Res.* **24**, 434 (1965).

8. PROCESS CONTROL. (By P. Harrioh, McGraw-Hill Book Co. Inc. New York, 1964) Doraiswamy, L. K. *J. Sc. Industr. Res.* **24**, 438 (1965)

9. KUNSTLICHE ORGANISCHE FARBESTOFF UND IHRE ZWISCHENPRODUKTE. (By H. R. Schweizer, Springer-Verlag, Berlin, 1964) Venkataraman, K. *J. Sc. Industr. Res.* **24**, 314 (1965)

10. RECENT ADVANCES IN AEROSOL RESEARCH. (By C. N. Davies, Pergamon Press Ltd., Oxford, 1964) Biswas, A. B. *J. Sc. Industr. Res.* **24**, 199 (1965).

11. CHEMISTRY & BIOCHEMISTRY OF PLANT PIGMENTS. (Edited by T. W. Goodwin, Academic Press Inc., New York, 1965) Venkataraman, K. *J. Sc. Industr. Res.* **25**, 79 (1966).

12. RAPID MIXING AND SAMPLING TECHNIQUES IN BIOCHEMISTRY. (Edited by B. Chance, R. H. Eisenhardt, Q. H. Gibson & K. Karl Longberg-Holm, Academic Press Inc., New York, 1964) Jagannathan, V. *J. Sc. Industr. Res.* **25**, 82 (1966).

13. ADVANCES IN HETEROCYCLIC CHEMISTRY, Vol. 4. (Edited by A. R. Katritzky, Academic Press Inc., New York, 1965) Venkataraman, K. *J. Sc. Industr. Res.* **25**, 129 (1966)

14. OPTICAL ROTATORY DISPERSION AND CIRCULAR DICHROISM IN ORGANIC CHEMISTRY. (By P. Crabbe, Holden-Day Inc., San Francisco, 1965) Sukh Dev *J. Sc. Industr. Res.* **25**, 90 (1966).

15. ORGANOMETALLIC SYNTHESIS, Vol. 1, TRANSITION METAL COMPOUNDS. (By R. B. King, Academic Press, Inc., New York, 1965) Subbaraman, P. R. *J. Sc. Industr. Res.* **25**, 90 (1966).

16. OPERATION MECHANISMS. (By T. A. Turney, Butterworths London, 1965) Doraiswamy, L. K. *Chemical Age of India*, **17**, 69 (1966).

Patents Sealed

1. **45666**

   Manufacture of nicotine sulphate from tobacco waste.
   Gedeon, J. and Goswami, M.

2. **47439**

   A process for the manufacture of mixed N. P. fertilisers.
   Gadre, G. T. and Gupta, J.

3. **53636**

   Improvements in or relating to coating compositions.
   Sarin, K. K. and Kapur, S. L.

4. **54867**

   A process for the manufacture of nicotine sulphate from tobacco and tobacco wastes.
   Bijawat, H. C., Razdan, R. and Potnis, G. V.

5. **55171**

   Treatment of CNSL for use in electrical insulating varnishes.
   Thakkar, K. P. and Gupta, J.

6. **55546**

   Improvements in or relating to ion-exchange materials.
   Ramakrishnan, C. S. and Krishnaswamy, N.

7. **55757**

   A process for the preparation of long-chain unsaturated ketones and 1-ω-keto-dicarboxylic acids from the said ketones.
   Menon, B., Nayak, U. G., Razdan, R., Chakravarti, K. K. and Bhattacharyya, S. C.

8. **56391**

   A process for the manufacture of civetone dicarboxylic acid (8 keto-pentadecane 1 : 15 dicarboxylic acid).
   Nayak, U. G., Chakravarti, K. K. and Bhattacharyya, S. C.

9. **56725**

A new process for the purification of selenium.
Sen, D. N. and Gupta, J.

10. **56726**

Preparation of water dispersible DDT as an oil bound paste.
Rao, K. V. N., Bhide, S. P., Kulkarni (Miss), S. B. and Biswas, A. B.

11. **57888**

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

12. **58868**

A process for the preparation of azelaic acid semiester suitable for making civetone dicarboxylic acid.
Nayak, U. G., Chakravarti, K. K. and Bhattacharyya, S. C.

13. **59419**

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

14. **59497**

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

15. **59606**

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

16. **59608**

Porous rigid filters.
Kapur, S. L. and Pandaya, R. N.

17. **59853**

Improvements in or relating to the preparation of costus root oil and the isolation of lactonic constituents therefrom.
Kelkar, G. R. and Bhattacharyya, S. C.

18. **59927**

A process for the preparation of pentadecane 1 : 15–dicarboxylic acid or its ester suitable for the preparation of dihydrocivetone.
Nayak, U. G., Chakravarti, K. K. and Bhattacharyya, S. C.

19. **60555**

Production of liquid rubber.
Uma Shankar.

20. **60826**

Improvements in or relating to the production of hydroxy, alkoxy or aryloxy substituted deoxybenzoins and particularly of deoxyanisoin.
Bose, J. L. and Shah, R. C.

21. **61585**

A process for the manufacture of an ammonium phosphate-sulphate fertilizer.
Gupta, J., Sheshadri, K., Lobo, J. and Rao, M. N.

22. **62302**

A process for the preparation of 1-ω-ketodicarboxylic acid (or ester) suitable for the preparation of civetone and dihydrocivetone.
Chakravarti, K. K. and Bhattacharyya, S. C.

23. **62890**

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

24. **63083**

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

25. **63736**

A liquid-liquid extraction procedure for the separation of niobium-tantalum oxide mixtures.
Sarma, B. and Gupta, J.

26. **64958**

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

27. **64959**

A Process for the preparation of dihydrojasmone.
Amin, J. H. and Bhattacharyya, S. C.

28. **65440**

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

29. **65543**

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

30. **65777**

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

31. **65778**

Improvements in or relating to the production of transdiethylstilbestrol dimethyl-ether and allied stilbenes.
Joshi, C. G., Bose, J. L. and Shah, R. C.

32. **65976**

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

33. **66096**

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

34. **66194**

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

35. **66803**

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

36. **66836**

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

37. **66966**

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

38. **67490**

Preparation of adhesive tapes.
Kapur, S. L. and Rao, B. R. K.

39. **67513**

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

40. **68611**

A new device for generating electrical power from the atmosphere.
Momin, A. U.

41. **70670**

Improvements in or relating to the controlling of water evaporation for conserving of water in lakes and reservoirs.
Kulkarni (Miss), S. B., Gharpurey, M. K., Deo, A. V., Sanjana, N. R., Abraham, K. O. and Subba Rao, B. C.

42. **71063**

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

43. **71190**

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

44. **72425**

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

45. **73702**

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

46. **74356**

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

47. **74451**

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

48. **77080**

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

49. **77081**

Improvements in or relating to the preparation of polyamide compounds and their compositions as antipriming agents in steam generators.
Pathak, K. D. and Subba Rao, B. C.

50. **77224**

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

51. **77225**

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

52. **82189**

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

53. **82822**

A process for the manufacture of high alpha cellulose dissolving grade pulps by alkaline pulping methods.
Vyas, G. M., Bendale, D. S. and Mahajan, M. B.

54. **83364**
Manufacture of hexachloroethane.
Bhat, N. A., Goswami, M. and Pai, M. U.

55. **83716**
Manufacture of nicotine sulphate from tobacco and tobacco wastes.
Potnis, G. V., Goswami, M., Ramachandran, V. and Pai, M. U.

56. **85446**
Preparation of carboxylic cation exchange materials.
Krishnaswamy, N., Indusekhar, V. V. and Dasare, B. D.

57. **85789**
Utilization of groundnut shells for the manufacture of high alpha cellulose dissolving grade pulp and vanillin.
Vyas, G. M., Bendale, D. S., Mahajan, M. B., Bose, J. L., Modi, B. D., Sonawane, H. R. and Bigg, D. C.

58. **86541**
A reactor for carrying out highly exothermic and explosive reactions particularly suited for chlorination of methane.
Mukherjee, S. P., Deshpande, A. D., Potnis, G. V. and Pai, M. U.

59. **86638**
A process for the preparation and synthesis of 2-iso-propenyl hexanols.
Ramaswami (Mrs.), S., Ramaswami, S. K. and Bhattacharyya, S. C.

60. **86991**
Preparation of polyurethane printing rollers.
Ghatge, N. D. and Kapur, S. L.

61. **89004**
A polycrystalline p-n junction photovoltaic solar cells.
Momin, A. U. and Sinha, A. P. B.

62. **90574**
A process for the preparation of dl-muscone.
Nair, M. S. R., Mathur, H. H. and Bhattacharyya, S. C.

63. **95075**
Utilization of groundnut shells for the manufacture of vanillin.
Vyas, G. M., Bendale, D. S., Mahajan, M. B., Bose, J. L., Modi, B. D., Sonawane, H. R. and Bigg, D. C.

64. **95076**

Improvements in or relating to the manufacture of lignin.
Vyas, G. M., Bendale, D. S., Mahajan, M. B., Bose, J. L., Modi, B. D., Sonawane, H. R. and Bigg, D. C.

Patents filed

1. **81071**

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

2. **81072**

Improvements in or relating to the preparation and production of catalysts for the hydrogenation of organic substances with particular reference to fatty oils.
Murthy, M. N. S. and Biswas, A. B.

3. **90677**

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

4. **91412**

Manufacture of 2, 3-hydroxynaphthoic acid from 2-naphthol in the presence of a dispersent.
Phadtare, P. G., Srinivasan, K. R., Baliga, B. A., Kotasthane, M. G. and Doraiswamy, L. K.

5. **92977**

Improvements in or relating to the manufacture of hexachloroethane.
Mukherjee, S. P., Goswami, M., Soundararajan, S., Sen, R. K. and Doraiswamy, L. K.

6. **94766**

Improvements in or relating to the preparation of jatamansi root oil and isolation of a coumarin constituent therefrom.
Unni, I. R., Maheshwari, M. L., Paknikar, S. K. and Bhattacharyya, S. C.

7. **96663**

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

8. **96801**

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

9. **97190**

Improvements in or relating to extraction or similar processes. (related to one of the steps in the processing of opium)
Narsimhan, G. and Shah, C. M.

10. **98153**

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

11. **98155**

Improved method for the hydration of sulphonation mixtures of copolymer beads.
Kapur, S. L. and Ramakrishnan, K.

12. **98156**

Preparation of solvent modified copolymer by suspension polymerisation of vinyl monomers.
Kapur, S. L. and Ramakrishnan, K.

13. **99589**

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

14. **99590**

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

15. **101161**

Process for the preparation of daylight and pink light emitting electroluminiscent phosphors.
Ambardekar, D. S. and Biswas, A. B.

● ● ●

Published by : Dr. B. D. Tilak, Director, National Chemical Laboratory, Poona 8.
Printed by : Shri D. V. Ambekar, at Aryabhushan Press, Poona 4.