NCL

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NATIONAL CHEMICAL LABORATORY ,

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C O N T E N T S

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BIOCHEMISTRY

I. STEROID SYNTHESIS

The isolation and screening of micro-organisms was undertaken for the selection of strains suitable for the production of intermediates for the synthesis of steroid hormones from cheap sterols. Forty-five strains were isolated from enrichment cultures containing cholesterol or sitosterol and examined for their capacity to oxidize or modify the side chain of the sterols. Three conversion products of cholesterol were isolated and are being studied. A few soil micro-organisms were also isolated from enrichment cultures containing the steroidal acids obtained by the chromic acid degradation of sitosterols. Seventeen cultures were screened for their ability to hydroxylate the nucleus of progesterone and fourteen of them were found to produce 11-α-hydroxy-progesterone together with varying amounts of more polar transformation products.

II. SULPHUR METABOLISM

The microbiological production of sulphur was developed to a semi-continuous process, starting from initial trials on raw sewage sludge, digested sludge from methane fermentation tanks, and inorganic sulphate. At the initial stage subcultures were carried out at progressively shorter periods for obtaining active mixed culture. After seven subcultures the formation of hydrogen sulphide was of the order of 1.4 g. per litre in seven days, and sulphide yields of 0.4 to 0.46% per raw sludge (w/v) per day were obtained. In

to 0.6 to 0.9% (w/v) by the continuous removal of hydrogen sulphide by a current of nitrogen. Work on the optimum conditions for the production of hydrogen sulphide and the use of other raw materials is in progress.

The formation of inorganic phosphate from ATP by D. desulfuricans was found to be due to three distinct enzyme systems acting without added substrate, with sulphite and tungstate respectively. The last enzyme was obtained in a highly active, soluble form.

A soluble preparation from D. desulfuricans of hydroxylamine reductase which catalyses the reduction of hydroxylamine by hydrogen was found to require hydrogenase, bacterial cytochrome, and possibly a third component. At pH 4.0 hydroxylamine reduction ceased, but the reduction of methylene blue was unaffected, indicating the possible presence of a specific hydroxylamine reductase.

III. PROTEIN CHEMISTRY

(a) Casein phosphopeptone

Ultracentrifugal studies on 6.66 M urea solutions of α and β caseins and phosphopeptones (paranuclein) and the determination of their sedimentation constants and molecular weights are in progress.

(b) Shark ray elastoidin

The peptide mixture obtained from the peptic digest of elastoidin was separated into two components on paper chromatograms. These two peptides were found to contain the following amino acids :

aspartic acid, threonine, serine, glutamic acid, proline, glycine, alanine, tyrosine and phenylalanine.

(c) Proteases of fungi

The kinetics and properties of the purified proteases from two strains of Aspergillus flavusoryzae were studied. The optimum pH with casein was 6 to 8 while there were two optima with gelatin at pH 7 and 10. The enzymes showed dipeptidase activity with leucyl glycine and glycyl glycine (Co^{++} activated) and tripeptidase activity with leucyl glycyl glycine.

(d) Molecular weight determinations

Weight average molecular weight (Mw) determinations from sedimentation velocity data were standardized with crystalline bovine plasma albumin and the values of Mw obtained by the methods of Baldwin (1927) and William et al. (1954) were found to agree with the data in literature. However, these methods failed to give reproducible results with gelatin systems. The sedimentation equilibrium technique of Kegeles et al. (1957) was therefore standardised with albumin and the determination of Mw of gelatin by this prodedure is in progress.

In order to determine whether the action of trypsin at high dilutions on gelatin is a degradation or merely a disaggregation of the molecule, the sedimentation behaviour of trypsin-treated and untreated gelatin was studied in the presence or absence of potassium thiocyanate. The results showed that the molecular size of samples treated with even trace amounts of trypsin for short periods was lower than

enzyme treatment.

(e) I.C.M.R. Enquiry on "The Metabolic Fate of Gelatin Administered as a Plasma Substitute"

The rate of excretion in urine and percentage retention in blood of gelatin samples of different average molecular weights is being investigated. Studies on the effect of transfusion gelatin on the maintenance of nitrogen balance and the formation of haemoglobin and plasma protein in doubly depleted dogs and rats are in progress.

IV. SYNTHESIS OF RESEARCH CHEMICALS AND C^{14}-LABELLED COMPOUNDS

(a) Biosynthesis of C^{14}-formate

The reduction of $C^{14}O_2$ by hydrogen to formate was carried out with E.coli cells grown on formate. About 15 to 22 per cent of the initial CO_2 was found to be reduced to formate and the residual CO_2 was recovered quantitatively. Pure labelled formate was obtained from the reaction medium in a yield of 80 to 90 per cent.

(b) Carboxyl-labelled acetate

Using a special gas circulating apparatus, which does not require liquid air as in the conventional vacuum line, acetate was obtained in 85 to 90% yield by the reaction of CO_2 with an ethereal solution of methyl magnesium iodide in non-isotopic pilot runs.

V. NATIONAL COLLECTION OF INDUSTRIAL MICRO-ORGANISMS

(a) Maintenance

The routine subculturing and maintenance of yeasts, bacteria and fungi in the collection were continued.

Cultures were regularly made available for the Biochemistry Division projects on the production of sorbose and amylase and for microbiological assay work. A total of 165 cultures were supplied to various institutions in India. Thirty-one new cultures including twenty-five actinomycetes were added to the culture collection.

(b) Screening for new organisms

i. Vitamin B_{12}

Isolation of cultures of actinomycetes from local soil samples was continued and 73 isolates were screened for Vitamin B_{12} production. Eleven samples of antibiotic culture broths obtained from the Hindusthan Antibiotics Ltd. were also assayed for B_{12} activity. Yields ranged from 0.2 to 1.2 mg/l., while with one of the isolates a yield of 2 to 2.5 mg./l. was obtained. Studies on variations in cultural conditions and screening of new isolates are in progress.

ii. Citric acid fermentation

Initial carbon dioxide levels of 0.1 to 0.5% in the atmosphere were found to accelerate markedly the germination of A. niger spores in modified Currie's medium.

The yield of citric acid with different samples of jaggery was found to vary between 40 and 60%. The effect of different methods of purification of jaggery for citric acid production is being studied. Mutants obtained by ultraviolet irradiation are under study in order to develop a suitable culture more tolerant to variations in trace element composition of the medium.

iii. Vitamin B_2

After a preliminary screening of different micro-organisms and various raw materials as substrates, a strain of Erymothecium ashbyii was found to give good yields of riboflavin on a groundnut-jaggery-cornsteep liquor medium. The effect of substrate concentration and intermittent addition of carbohydrates was studied. Yields of about 700 mg/l. were obtained in preliminary experiments.

PILOT PLANT PROJECTS

I. TRANSFUSION GELATIN

Preliminary pilot plant batches of transfusion gelatin were prepared and were found to be as effective as the laboratory scale preparations in physiological trials with splenectomized dogs, which were carried out in collaboration with the Armed Forces Medical College, Poona.

The preparation of ten batches of transfusion gelatin was undertaken for the determination of the reproducibility of the process on a pilot plant scale and for clinical trials. Five batches of ossein were prepared out of which three batches were further processed for the preparation of about 500 bottles of gelatin solution. The physical and chemical properties of the material were found to conform to those of preparations obtained on a smaller scale. The physiological testing of this material is in progress.

II. VITAMIN C SYNTHESIS (In collaboration with the Chemical Engineering Division)

After small-scale laboratory trials the synthesis of vitamin C was carried out on a 1-lb. scale and then on a 10-lb. scale. Six 1-lb. batches of Vitamin C were prepared and the yields obtained in small-scale experiments were found to be reproducible on the 10-lb. scale. About 40 lbs. of pure crystalline Vitamin C were prepared. The final material was found to conform to all the pharmacopoeia tests and was non-toxic to rats when fed at a high level (150 mg/kg. of body weight). The yields were generally of the same order as in the small scale trials. Some minor modifications were made in the process on the basis of the pilot scale work.

III. BACTERIAL DIASTASE

A total of thirteen bacterial fermentations were carried out on a 20-litre scale and reproducible results were obtained. The enzyme was precipitated in 85-90% yield by precipitation with either ammonium sulphate at room temperature or with alcohol at 0^{o}. The relative efficiencies of recovery of the enzyme from the fermented medium by three different procedures, by direct drying of the medium or by precipitation with alcohol or ammonium sulphate, are being studied on a pilot plant scale in collaboration with the Chemical Engineering Division. Supplementation of the medium with soluble starch, peptones, casein hydrolysate, amino acids and other growth factors, the use of spores instead of active growing cultures as the inoculum and other variations in the experimental conditions were tested in shake flasks and in the 40-litre fermenter,

but no significant increase in activity was observed. Twenty commercial samples of diastase were tested and it was found that in laboratory tests the preparations obtained in the pilot plant experiments were comparable in activity with the commercial samples.

TECHNICAL AID

Assistance in the form of technical advice, analytical reports or supply of samples was given on the following problems :

(1) Ultracentrifugation of influenza virus preparations for the Armed Forces Medical College, Poona and of enzyme preparations for the Hindusthan Antibiotics Ltd. (2) Paper chromatographic analyses of pathological urine samples for the Military Hospital, Poona.(3) Assistance to Dr. Modi, Baroda University, on the study of fermentation technology. (4) Ultracentrifugal and electrophoretic runs for the Biochemistry Section, University of Poona and the Armed Forces Medical College, Poona.(5) Laboratory facilities extended to Dr. A.G.Chitale of the Ahmedabad Textile Industry's Research Association, Ahmedabad.

CHEMICAL ENGINEERING

I. POLYVINYL CHLORIDE PROJECT

The bench-scale investigations on the four-stage process for the production of PVC from alcohol and chlorine were concluded with the completion of the polymerization studies. Further investigations on the

effect of temperature and concentration of suspending agent (PVA) respectively on the properties of polymer samples were carried out.

Work on the pilot plant, which had just been started, was continued this year. It is designed for an output of about 5 lbs. of ethylene per hour and has corresponding capacities for the subsequent products, and is expected to finally yield about 8-10 lbs. of PVC per hour.

The integrated compact pilot unit for the first stage of the process (catalytic dehydration of alcohol) was completely assembled. Preliminary tuning runs indicated the need for certain modifications, particularly in the design of the reactor to enable smoother working. The plant could be ultimately operated satisfactorily to deliver a product gas analyzing 97-98% of ethylene, with conversions well over 90% at the designed capacity of about 5 lbs. of ethylene per hour. Detailed investigations, covering about 70 useful runs, were then carried out to study the kinetic performance of the reactor, and also gather related engineering data. Runs were made at selected temperatures in the range of 350°C to 450°, using different space velocities and catalyst weights respectively. The effect of concentration of the feed alcohol on conversion was observed to be not very significant under comparable conditions even when the strength of alcohol was varied from 95% to 50%. Attempts will be made to work out suitable rate equations for reactor scale-up.

The pilot plant for the second stage (production of ethylene dichloride from ethylene) was installed. This essentially consists of a turbo-absorber reactor, a liquid-liquid continuous stirred tank washer, a coalescer, intermediate storage tanks and pumps, interconnected by suitable pipe flow lines. The whole assembly has been so arranged and integrated with the ethylene unit that ethylene dichloride may be produced directly and continuously from alcohol and chlorine. A continuous rectification equipment was also designed, fabricated in the NCL workshop, and assembled for producing refined ethylene dichloride. Some minor improvements were made to rectify certain fabricational defects of the chlorination reactor after carrying out initial runs. Regular runs for producing ethylene dichloride and collecting the performance data will be started shortly.

The lay-out plans for installing the pilot plant for the third stage for the production of vinyl chloride by the thermal dehydrochlorination of ethylene dichloride have been prepared, and the plant will soon be erected.

Experimental and theoretical work on certain related problems was also carried out. Data on the process kinetics of thermal dehydrochlorination of commercial ethylene dichloride in stainless steel tubes were required, but suitable published information was lacking. Investigations were carried out to determine the effect of temperature and space velocities on the conversion and product distribution in the thermal dehydrochlorination of ethylene dichloride at various temperatures in the

was carried out and yields were determined. The results generally indicate that the subsequent decomposition of the formed vinyl chloride was not great at temperatures below 500°. The necessary thermodynamic data for the various reactions involved in this process are being gathered and the kinetic data will then be examined.

The thermodynamic properties of vinyl chloride are useful in the calculation of energy requirements for the compression and distillation of vinyl chloride. These were computed from the limited available experimental data and by using the generalized "reduced-state" procedure. The temperature-enthalpy and temperature-entropy charts suitable for engineering purposes have been prepared.

Thermodynamic data for the catalytic dehydration of alcohol to ether and ethylene have been calculated. Preliminary work on certain other problems such as the comparison between the fixed and fluid beds for catalytic dehydration of alcohol, and a study of coated catalysts for the catalytic dehydrochlorination of ethylene dichloride to vinyl chloride have been started.

II. VITAMIN C PROJECT (See also under Biochemistry Division)

Pilot plant experiments were carried out with available equipment after necessary modifications. The design of a self-contained unit and of a unit for commercial production on a scale of 1 cwt. per day is in progress.

III. PREPARATION OF SORBITOL FROM GLUCOSE

Work on this problem has been started principally in connection with the Vitamin C project, for which

Very pure sorbitol is required for vitamin C synthesis, but lower grades of sorbitol have a variety of other uses.

The reaction involved is the catalytic reduction of glucose or starch hydrolysates by hydrogen under pressure. Preliminary work was started in a rocking autoclave of about 2-2½ litres capacity, using copper chromite and Raney nickel catalysts at 100 to 160° and 25 to 120 atm. pressure. It is now proposed to carry out a detailed process study with Raney nickel catalyst in the first instance.

A 5-gallon medium pressure hydrogenation reactor has been designed and attempts are being made to get it fabricated in India. It is also hoped to procure a continuous hydrogenation reactor assembly from foreign sources. Other high pressure accessories, such as a small manually operated booster compressor, and valves, are being fabricated in the NCL workshop.

IV. EXTRACTION OF NIM OIL

Detailed studies on the pilot plant liquid-liquid extraction of nim oil by alcohol for complete removal of its bitter constituents, sulphur compounds and free fatty acids were started in connection with the project sponsored by the Organic Chemistry Division. Three techniques are being studied: (1) continuous counter-current extraction on a Podbielniak centrifugal liquid-liquid extractor, (2) batch extraction in stirred tanks, and (3) a combination of the two.

The alcoholic extracts are distilled and the bitter constituents are being recovered. About 400 lbs. of nim oil have been treated in these initial runs.

V. PRODUCTION OF COSTUS ROOT OIL

Pilot plant development of the process worked out earlier in the Essential Oils Section was started with a view to study the unit operations involved and also to treat about 1 ton of costus root in the first instance. The principal unit operation of solvent leaching (solid-liquid extraction) of costus root oil by redistilled petroleum ether at room temperature is being intensively studied. Initially the grinding characteristics of costus root, from the Punjab and Kashmir were approximately determined in a rotary knife cutter and in a heavy duty hammer mill. Samples of the powder were sieve-analysed and the oil content of each fraction and of the composite powder were determined. Preliminary work was also carried out on the equilibrium distribution of oil between the solid residue and the solvent. Suitable quantities (40-80 lbs. per batch) of costus root powder were used in studies on the pilot scale extraction, and for the simultaneous production of costus root oil. Three such batches of 40 lbs. and three of 80 lbs. each were treated. The effect of certain variables, such as particle size of powder, method of extraction, duration of extraction, and solvent-solid ratio, are being investigated. The extracts are distilled under vacuum below 40° to obtain the oil. About 20 lbs. of good quality oil have been extracted so far.

VI. PILOT PLANT WORK ON HEXACHLOROETHANE

Laboratory scale investigations on the direct one-step production of hexachlorethane from ethelene and chlorine in a glass reactor using a 500 c.c.

catalytic bed were carried out some time ago. Designs of equipment for a pilot plant with a capacity of about 5 lbs. of hexachloroethane per hour have now been prepared, and some of the simpler units are being fabricated in the NCL workshop. A multi-tube oil-heated catalytic reactor is the principal unit in the assembly and detailed designs have been sent to fabricators in the country. Some pre-pilot plant investigations on the effect of the material of construction on quality of the product and on the corrosion of the reactor are now being carried out. Although nickel was found to be the most suitable material of construction, alternative materials such as nickel-coated copper are being examined because of the supply position.

VII. BENCH SCALE STUDIES ON THE DIRECT-OXIDATION AND CHLORINATION PROCESSES FOR PRODUCTION OF ETHYLENE OXIDE

Ethylene oxide is a versatile raw material for the synthetic production of many useful organic chemicals. It is manufactured from ethylene by two main processes : (1) direct oxidation with silver oxide as catalyst, and (2) via the chlorhydrin. Preliminary experiments on both these methods using glass reactors are in progress.

VIII. PULSED PACKED COLUMN

This investigation on pulsed packed columns. was started in continuation of the study of mass transfer in these columns carried out earlier. A suitable column of 2½" i.d. was set up with arrangements for feeding the lighter and heavier phases. The effect of various factors such as the frequency and amplitude of pulses, of the viscosity and density of the continuous phase, and of

interfacial surface tension are being studied to test the hydrodynamic characteristics of the column. The frequency varied between about 25 and 60 cycles per minute and amplitudes between 4 and 9 mm. Solutions of glycerine of different concentrations have been used as the continuous phase and benzene as the discontinuous phase. A large number of runs have been carried out and the data are being gathered to work out a design equation. It is considered desirable also to study the effect of different packings.

IX. PRODUCTION OF SEBASIC ACID AND OCTANOL-2 FROM CASTOR OIL (in collaboration with the Organic Chemistry Division)

A small batch reactor and accessories for carrying out the reaction using castor soap as the starting material has been designed. The design of a continuous system is under consideration.

X. PREPARATION OF 10-UNDECENOIC ACID AND HEPTALDEHYDE FROM CASTOR OIL (in collaboration with the Organic Chemistry Division)

A small bench-scale unit for the continuous thermal cracking of castor oil has been designed and is being fabricated in the NCL workshop. A partial condenser to avoid fractional distillation has been incorporated in the design.

XI. MISCELLANEOUS PROBLEMS

The following miscellaneous problems have been studied : (1) settling rate of sludges, (2) effective thermal conductivity of packed beds, (3) kinetics in the solid-liquid-gas systems, (4) heat transfer during combustion of a fuel droplet, (5) behaviour of some non-newtonian polymer solutions and (6) drying of heat-sensitive materials.

XII. PHYSICO-CHEMICAL CHARACTERISTICS OF INDIAN LIMESTONES AND LIMES

Work on the second batch of Indian limestones was continued. Six more samples of Indian limestones were taken up for study, thus making a total of 24 samples for the second phase of the work.

Detailed chemical analyses of these six limestones were carried out. Various physical properties of the limestones and of the lime, obtained by calcining the limestones at 1000° were determined. The calcination rates of these limestones were also studied using 1" cubes in a muffle furnace. Some of the characteristics of the hydrated limes, such as the constant setting rates of sludge and percentage conversion of sodium carbonate with the use of these limes, were investigated. Certain interesting observations were made for the settling characteristics of milk of lime suspension. The leather industry prefers a slow settling suspension in order to maintain as high a concentration of the lime solution as possible. Changes in the settling characteristics of the limes were observed on keeping the sludge for some time and reforming the suspension, but the reasons are not clear.

The project has now been completed and the second monograph on high calcium limestones of India has been written up for publication.

XIII. CARBON BLACK PROJECT

The carbon black samples, obtained by the continuous operation of the small pilot plant as reported last year, were tested according to standard procedures. Initially

shaking them with toluene. About 40 samples were then selected for further detailed testing to determine (1) percentage of moisture, (2) percentage volatile matter, (3) percentage toluene extract, (4) nigrometer index, (5) pH of the water extract, (6) D.P.G. adsorption, (7) particle diameter by electron microscope measurements, (8) percentage grit, (9) ash per cent, and (10) iodine absorption. Some of the samples were then compounded in natural rubber according to the standard test procedure, and the products were tested for tensile strength, modulus, ultimate elongation, Shore hardness and abrasion loss.

The investigations carried out till now on this project generally indicated that the furnace black process of carbon black manufacture is flexible, and it may be possible to operate a plant to produce different grades of carbon black with varying degrees of fineness and other characteristics from different feedstocks. It also indicated that the furnace blacks consumed by the rubber industry could probably be manufactured from the indigenously available petroleum tar oils. A detailed report incorporating the results was written up, and the project was concluded.

XIV. CHLORINATION OF ILMENITE

In connection with the design and assembly of a continuous fluidized bed reactor for the preferential removal of iron by chlorination of ilmenite, residues which were practically free of iron oxide were prepared by carrying out the chlorination of ilmenite initially in a batch fluidized bed. These residues were meant for blending with the original ilmenite ore to obtain a suitable initial charge for the continuous reactor with a pre-determined iron oxide content of the charge. Meanwhile a continuous feeder

for the fluidized reactor was fabricated by the workshop. Several trials were carried out with it, but due to the highly erosive nature of the mineral particles, it did not function satisfactorily. The results obtained in the kinetic study of the batch fluidized chlorination of ilmenite have been communicated for publication. The project has been terminated.

XV. COMPARATIVE STUDY OF THE METHODS OF DRYING GELATINE FROM HIDES OR BONES

Initial experiments on a Mitchell vacuum double-drum drier with two cylindrical drums (6" long x 6½" i.d.) showed the feasibility of drying gelatine solutions by this process. Systematic studies were carried out to investigate the effect on product quality of (1) concentration of the gelatine solution, (2) steam pressure in the drums and (3) speed of the drums, the vacuum being kept constant throughout the series of experiments.

The samples obtained were tested for their important properties, such as (1) moisture content, (2) melting point, (3) viscosity, and (4) jelly strength. The project has been terminated.

XVI. MISCELLANEOUS WORK

(a) Considerable ground has been covered for the organisation of the rayon-grade pulp project. A meeting of the Progress Reviewing Committee of the Cellulose Research Committee considered and approved the requirements of staff and equipment. Detailed specifications for the viscose and spinning units were finalised after extensive correspondence. A study visit to Gwalior Rayons, Nagda, was made. The indent for these two units has been placed with the DGS & D.

(b) The project for the construction of the chemical engineering pilot plant building was taken up again. The plans prepared earlier were altered in the context of present requirements and discussed with the CSIR architect.

(c) The out-door laboratory adjoining the furnace shed has been converted to a High Pressure Autoclave Room.

(d) Designs for two reactors required for the production of CNSL-based ion-exchangers were prepared for the Plastics & Polymers Division.

(e) Approximate cost estimates were made for (a) chloroform by alternative routes, (b) disastase, (c) β-ionone and (d) chlorination of bauxite sludge.

INORGANIC CHEMISTRY

I. HEAVY CHEMICALS

(a) Titanium dioxide from bauxite sludge

The chlorination of bauxite sludge, a waste product of the Indian Aluminium industry, was carried out by upgrading the sludge with hydrochloric acid, briquetting the upgraded sludge with powdered charcoal, drying the briquettes at 600° and chlorinating at 400°-500°. Over 90% of the titania in the briquettes was removed as titanium tetrachloride with chlorine efficiency of about 60%. Hydrolysis of the tetrachloride produces rutile type titania, a pigment superior to the anatase type which is produced by M/s. Travancore Titanium Products Ltd., from ilmenite. The chlorination of ilmenite presents difficulties, because of the economic and engineering problems involved in

separating iron chlorides. In the United States titanium tetrachloride is manufactured from imported rutile, and not from domestic ilmenite.

The chlorination of bauxite sludge which contains about 15% ferric oxide with 20% titanium dioxide appears to be impracticable without the necessary upgrading. On the other hand, much hydrochloric acid is required to remove ferric oxide to a considerable degree and this will make the process uneconomical. A process was therefore developed for upgrading the sludge, in which the quantity of hydrochloric acid used was only the amount available during the hydrolysis of titanium tetrachloride. By heating the sludge with carbon at 900°-950° in a closed container and treating with the stated amount of hydrochloric acid, the ferric oxide content was reduced to only 2.4%, while titanium dioxide went up to 37%. This sludge was briquetted without any further addition of carbon and was then chlorinated at 400-450°. Further work to solve some technical problems may be carried out in collaboration with M/S. Aluminium Corporation of India Ltd., who have shown interest in this project.

(b) N-P fertilisers

A new process for the manufacture of ammonium phosphate-sulphate fertiliser (Ammophos II) has been worked out, and a patent application(No. 61585) filed. It uses ammonium bisulphate in place of sulphuric acid for solubilising P_2O_5 of rock phosphates. Iron, calcium, silica, etc., are left insoluble, giving a water-soluble crystalline powder containing N 16-18, P_2O_5 23-25 per cent. Ammonium bisulphate may be obtained either by mixing

acid, or by heating ammonium sulphate to 350-400°. The process is also applicable to high-iron phosphatic rock like Singhbhum rock phosphate, and reduces the consumption of sulphuric acid for the manufacture of phosphatic fertilisers in the country. Various factors governing the efficiency of the process have been studied in detail to provide basic laboratory data to interested manufacturers. Gypsum sludge, an important byproduct of the process, can be used in the fixation of ammonia to ammonium sulphate.

Concurrently, some further study was made on our old patent No.47439 (June, 1952), which describes a process for making a mixed fertiliser from rock phosphate, ammonium sulphate and hydrochloric acid. By substituting ammonium sulphate with ammonium sulphate-nitrate, non-caking products of 8-13, 11-11 and 15-8 (N-P_2O_5) compositions could be prepared. With ammonium carbonate in place of the sulphate, the availability of P_2O_5 in the fertiliser went down, while urea gave a hygroscopic product. The original patent describes a friable product of the composition N 7, P_2O_5 15 (availability 85-90%) per cent.

(c) Synthetic cryolite

Some experiments were carried out on the extraction of fluorine from an upgraded sample of Indian fluorspar (78 per cent CaF_2) supplied by M/s. D.Saraf & Sons. Owing to the high silica content of the raw material, alkali extraction methods were ruled out because the permissible silica content in cryolite for aluminium manufacture is lower than 0.5%. Extraction studies were carried out mostly with aluminium sulphate, which is known

to form a soluble fluoro-sulphate complex when calcium fluoride is heated with a concentrated aluminium sulphate solution. It was found that fluorine was solubilised up to the extent of 80 per cent, and the solution was practically free from silica which makes it suitable for precipitating cryolite. Precipitation under various conditions, with or without the simultaneous addition of sodium aluminate, only gave mixtures of cryolite (30%) with alumina (70%). Attempts to separate the two constituents were not successful, nor can a mixture of such composition be directly added to the cryolite bath in aluminium manufacture. A direct distillation of constant boiling hydrofluoric acid from aluminium fluosulphate solution by heating with sulphuric acid gave poor yields. The problem is still under investigation, but it appears that aluminium sulphate may have to be replaced by some other extractant.

(d) Manganese dioxide for dry batteries

M/s. Estrela Batteries Ltd. having reported poor performance of the Shivrajpur ore as well as of the byproduct gamma-MnO_2 from M/s. Standard Chemical and Pharmaceutical Co. as compared to that of the Gold Coast ore, attempts were made to improve the properties of the Indian raw materials. On the basis of literature studies, the Indian materials were subjected to certain thermal and extractional treatments, and several dry cells were fabricated from used carbon rods of old dry batteries and zinc cans made in the Laboratory. Some sort of perforation was noticeable in all of them within a period of 2-3 months indicating heavy corrosion, which may be caused by the

solder used or some other less obvious factors. In a completely discharged cell it was found that 62% of MnO_2 is reduced to Mn_2O_3 when the cell was discharged continuously with 1.5 V lamp in series. The extent of this reduction at complete discharge was even less in an intermittently discharging cell, indicating in both cases that the full capacity of the depolariser could not be utilised.

II. FINE CHEMICALS

(a) Separation of the rare earths

In the year under review, much of the chemical work of separation involving oxidation, fractional hydrolysis, reclamation of rare earths and their recycle into the process to eliminate loss, etc., had to be repeated on an increasingly larger scale for collection of basic laboratory data and of suitable concentrates for final treatment by ion exchange processes. Completely continuous process flow-sheets were evolved for the preparation of pure ceria, and lanthana and didymia concentrates. The customary citrate elution technique on Dowex-50 resin was modified so as to increase the yield capacity of the resin for pure lanthanum by a factor of about 5. The principal feature of this modification is that, starting with a lanthana concentrate, the lanthanum is immobilised on the resin while the other constituents are fractionally eluted. In a somewhat modified manner, fractionation is also being carried out with comparatively large loads on the resin of the didymia concentrate.

The feasibility of separating the light lanthanons on anion exchange resins was also under investigation, the idea being an extension of a similar principle applied earlier to the separation of hafnium from zirconium. Anionic 'Enta' complexes, cracked with very weakly acidic solutions did not produce expected results. The anionic tripolyphosphate complex, however, on treatment with dilute mineral acids gives a fair separation of lanthanum, but Pr, Nd and Sm were not separated satisfactorily. Better results are generally obtained on cationic exchangers. The project is partly supported by a grant from A.E.E., Bombay.

(b) Separation of Zirconium from Hafnium

Essentially, there are two important but somewhat different problems associated with this project. The first and the more important one is to develop an efficient and quick method of isolating a zirconium compound containing less than .01% hafnia. The second is the isolation of a hafnium compound of a purity of about 99% or over. Both these products are of great value in atomic energy work.

The opening up of Indian zircon with alkali, and the subsequent preparation of a pure, natural mixture of zirconium and hafnium oxychlorides has been reported earlier. Starting from the iron-free oxychloride as the raw material, a new method of continuous isolation of hafnium-free zirconia has been developed on the principle of frontal elution on activated silica gel. The method has been under trial for some time, and has already yielded about half a pound of hafnium-free zirconia. More units are being set up. In addition to the pure zirconia, a rich

For the preparation of pure of high-grade hafnia, an anion-exchange method reported earlier is found to be the most suitable. The original method has been subjected to careful study with a view to arrive at an optimum efficiency commensurate with economic operation. The possibility of applying the method to hafnia concentrates (containing upto 30% HfO_2) in place of the natural mixture is being examined. Basic quantitative data are also being collected to understand the mechanism of the new process, i.e. whether the process involves a preferential cracking of the fluorocomplexes followed by the formation of other complexes in solution. Independent physico-chemical experiments are also planned to study the nature of anion-cation interaction in a fluoro-zirconate sulphuric acid system. The project is partly supported by a grant from the A.E.E.

(c) Separation of niobium from tantalum

The pure metal niobium has surpassed others in its suitability for cladding cores of fast reactors. India has good resources of niobium-containing minerals. Tantalum, which is invariably associated with niobium and is extremely similar to it in properties, must be separated, and is itself useful as a corrosion-resistant material of construction. Efficient separation of the two was long regarded a master problem in inorganic chemistry; but lately, some apprently good liquid-liquid extraction processes have been mentioned in foreign patents.

Preparation of the necessary raw material, a relatively pure mixed oxide of the two elements from the ores, is not difficult. We found it convenient to open the mineral with alkali, followed by an acid leach.

The liquid-liquid extraction method, using a water-immiscible organic solvent (a ketone in this case) has been developed. Pure tantalum goes in the organic phase, and the two are subsequently recovered by appropriate methods. About 80% of the organic solvent is recovered and recycled. Experiments upto a scale of 20 g. mixed hydrated oxide per batch have been carried out giving pure Nb_2O_5 ($Ta_2O_5 < 0.01\%$) and Ta_2O_5 ($Nb_2O_5 < 0.01\%$). High yield have been obtained in these small-scale experiments. A patent has been applied for.

(d) Organic titanium/silicon compounds

Organic esters of titanium have lately found a variety of industrial uses as water repellents, surface coating compounds, resin-cure accelerators and sizing agents for fibres. Among aliphatic esters, butyl titanate has been studied in detail and its properties are now well established. Butyl alcohol is not manufactured in the country, but fusel oil is available in large quantities as a byproduct of the alcohol industry. The fraction of the oil distilling between 105°-130° has been successfully used to prepare fusel oil titanate and fusel oil silicate, which are polymerisable like the butyl analogues. A method is also being developed for the preparation of fusel oil phosphate, since the corresponding butyl ester has found many important applications in extractive processes of purification of inorganic materials. All these products are now under examination as substitutes for the butyl derivatives.

Silicones and other organic silicon compounds are becoming increasingly important for their many and varied uses, e.g., as water repellents, foam suppressors, lubricants, and heat-resistant gaskets. The basic work in silicone chemistry is the preparation of the intermediates of the formula R_nSiX_{4-n}, the general method of synthesis being the well-known Rochow's process in which the organic halide vapour acts on powdered silicon in presence of a catalyst. Our first attempt to replace silicon (and the catalyst) with high-grade ferro-silicon, which is a product made in the country, showed that a reaction was possible, but the iron chloride formed choked the tube, stopping further reaction. To avoid choking troubles, the reaction was carried out with the ferro-silicon powder suspended in a high-boiling liquid. It was found that reaction did proceed in one or two cases, but the modification could not be a general method of preparation and a substitute for Rochow's procedure. For the synthesis of aromatic chloro-silanes, the Grignard reaction was found suitable.

III. ANALYTICAL METHODS AND TECHNIQUES

Consistent with the flexible nature of this project, greater emphasis during the year was on quantitative spectrography and polarography. Routine spectrographic estimations have greatly increased with the progress of certain preparative projects described earlier, making an extension and improvement in the present set-up somewhat necessary and urgent. After a detailed study of the relative intensities of line pairs of niobium and tantalum, a group of 9 pairs was selected for the estimation of Nb Ta and vice varsa in concentration ranges 0.1-1% and 1-30%. A large

A significant finding was the high stability of certain tripolyphosphate complexes of metals, which have possible application in analysis and in other ways. A polarographic reduction at the dropping mercury cathode of the uranium tripolyphosphate complex has been studied in some detail, based on which a polarographic method of estimation of uranium in presence of a large number of ordinarily interfering elements has been worked out.

ORGANIC CHEMISTRY

I. SYNTHETIC DRUGS

(a) Synthesis of stilbestrol and its analogues

Laboratory scale preparation of the important synthetic oestrogen, stilbestrol, has been completed, following the general route of Dodd's synthesis starting from deoxyanisoin. Some improvements and modifications were introduced.

A new method has been developed for the dehydration of the stereoisomeric forms of 3:4-dianisylhexan-3-ol to trans-stilbestrol dimethyl ether by which 90-98% of the required trans isomer is obtained almost exclusively in a single operation.

The preparation of 100 g. of stilbestrol dimethyl ether has been completed.

(b) Synthesis of anticoagulants of the dicoumarol series

4-Hydroxycoumarin is the key intermediate for the synthesis of important anticoagulant drugs such as dicoumarol, tromexan, sintrom and marcoumar which are extensively used in therapy, particularly in acute

coronary occlusion following thrombosis. It is also used as an intermediate for the synthesis of important rodenticides, such as warfarin and cumachlor. Two new processes have been developed for the synthesis of 4-hydroxycoumarin. The conditions leading to the optimum yield of 4-hydroxycoumarin prepared by one of these new methods were arrived at after systematically carrying out a large number of reactions in which temperature, time of reaction and proportion of the condensing agent were the variables.

A number of 4-hydroxycoumarins having substituents in various positions were prepared by the two new methods.

The unknown 5-methyl-8-isopropyl-4-hydroxycoumarin and the corresponding dicoumarol were prepared in view of their expected anticoagulant properties and have been sent to the G.S. Medical College, Bombay, for testing.

(c) Synthesis of pyridoxine (vitamin B_6)

Laboratory scale experiments have been carried out for the synthesis of this vitamin by the two main known routes, and improvements have been effected in the reduction stages.

II. STEROIDAL HORMONES

An efficient and simple method has been developed for the separation of sterols from sugarcane wax. Stigmasterol, has been converted in a four-step synthesis to progesterone, one of the female sex hormones. All the steps have been standardized in laboratory-scale experiments and progesterone has been obtained in an overall yield of 35%. Sitosterol has been oxidised to the valuable intermediate, dehydroepiandrosterone in 2% yield.

III. SYNTHESIS OF VITAMIN A

Using the C_{14}-aldehyde, purified through its semicarbazone, the synthesis of vitamin A acetate was accomplished.

IV. SYNTHESIS OF DITERPENOIDS

(a) A new total synthesis of ferruginol, a diterpenoid phenol, has been accomplished. The present synthesis is stereospecific and is an improvement on the earlier synthesis by F.E. King et al.(b)In connection with the synthesis of the $C_{12}H_{18}O_6$ tricarboxylic acid, a degradation product of abietic acid, the intermediate 5-methyl-5-carbomethoxydecalone-1 has been prepared.

V. CHEMICAL EXAMINATION OF MUNDULEA SUBEROSA

Rotenone has been isolated from the ether extract of the defatted seeds of Mundulea suberosa.

VI. ACONITE ALKALOIDS

On the basis of degradation and spectral data tentative structures have been assigned to the alkaloids aconitine and delphinine.

VII. SUGARCANE WAX

Samples of wax bleached with nitric acid were sent to (1) Bharat Carbon and Ribbon Manufacturing Co., Calcutta, (2) Central Leather Research Institute, Madras and (3) Small-scale Industries Institute, Madras, for testing. Five pounds of modified wax were also prepared and sent to the two latter institutes and to M/s.Reckitt & Colman for trials.

In the bleaching of crude wax with sodium dichromate and sulphuric acid, the requirement for dichromate was reduced by 35%.

VIII. PREPARATION OF PHENOL FROM CUMENE AND p-CRESOL FROM p-CYMENE

Phenol and p-cresol were obtained respectively from cumene and p-cymene in 75% yield by the hydroperoxide process. Further work was suspended after it was learnt from CSIR News that similar work is in progress at the Fuel Research Institute.

IX. PILOT PLANT WORK ON NIM OIL

Large scale alcohol extraction of nim oil is being carried out both by a batch process and by means of a Podbielniak centrifugal extractor. A number of experiments were carried out for alkali refining of alcohol-extracted nim oil in the De Laval Pilot Unit. The refining loss was found to compare favourably with that for other vegetable oils having high acid values. The refined neutral oil could be hydrogenated with commercial nickel catalyst. A few laboratory-scale experiments for bleaching of refined nim oil with activated earth and carbon have been carried out.

X. SODIUM NIMBIDINATE

Sodium nimbidinate was prepared by an improved method of hydrolysis under milder conditions and liberation of the acid by a cation exchanger. Sodium nimbidinate has been shown to be a useful diuretic in clinical trials carried out at the K.E.M. Hospital, Bombay. Attempts are being made to prepare a product of uniform biological activity.

XI. BITTER CONSTITUENTS OF NIM

Nimbin, the principal crystalline bitter constituent of nim oil, has been provisionally assigned the structure

XII. PAINTS AND VARNISHES

(a) Anticorrosive paints

The stability of some corrosion inhibitive pigments when incorporated in anticorrosive paints using different varnish bases was determined. Based on these studies, twenty paints were prepared and their water-resistance determined by the radioactive tracer method. Four of these paints showing good water-resistance were sent to the Naval Dockyard, Bombay, for raft-exposure tests.

Dehydrated castor oil long oil alkyd and dehydrated castor oil, linseed oil, long oil alkyd have been found to be useful as vehicles for fast-drying anticorrosive paints.

(b) Anti-fouling paints

Two copper benzoate-containing paints were prepared and their solubilities in sea-water under ordinary and accelerated conditions were determined.

(c) Silicone resins for heat resistant coatings

Thirteen silicone alkyd resins were prepared from epoxysilanes. Some of the compositions were heat- and water-resistant.

(d) Lacquers for food containers

Two of the four compositions intended for use as food can lacquers were found to be satisfactory in laboratory tests and comparable with an imported composition. Incorporation of cashewshell liquid-formaldehyde resin in some varnish compositions gave lacquers comparable with those available in the market. Tins coated with these lacquers have been sent to C.F.T.R.I., Mysore, for storage tests.

(e) Utilisation of modified kamala seed oil in surface coatings

Kamala seed oil modified by alcoholysis with butyl or amyl alcohol was used in various coating compositions of pure and modified phenolic resins, maleic resin, coumarone indene resin, ester gums, etc. Except for slightly lower resistance of the films to some organic solvents, these were quite comparable to the corresponding compositions prepared from tung oil.

XIII. STABILIZATION OF EDIBLE FATS

Several catechol derivatives were prepared for studying their antioxidant properties. 4-lauroylcatechol and 4-propionylcatechol were prepared in 70-88% and 70% yields respectively according to a new general method for the preparation of aryl alkyl ketones developed earlier in this Laboratory in which phenols are condensed with aliphatic acids in the presence of a mixture of phosphorus oxychloride and anhydrous zinc chloride.

4-Propylcatechol was prepared by Clemmensen reduction of 4-propionylcatechol. Hydrogenation of eugenol and subsequent demethylation gave very poor yields of 4-propylcatechol.

These synthetic products and catechin isolated from catechu are being tested for their antioxidant properties.

XIV. DIARYL KETONES FROM LONG CHAIN DICARBOXYLIC ACIDS

Work on the condensation of sebacic acid and hexadecamethylene-1:16-dicarboxylic acid with monohydric phenols and the Fries rearrangement of the diesters was continued. The diketones were converted to the corresponding hydrocarbons by Clemmensen reduction, and then sulphonated.

XV. MOLECULAR COMPOSITION OF KAMALA SEED OIL

The low glycerine content found in all the different fractions of kamala seed oil shows that a polyester of pure kamalolenic acid is probably not present in the oil, and besides the simple triglyceride molecules present to an extent of 12 per cent, most of the other components are complex triglycerides in nature.

XVI. PREPARATION OF FATTY ALCOHOLS FROM VEGETABLE OILS

Experiments have been carried out on sodium reduction and high pressure hydrogenolysis methods for the production of fatty alcohols, which have a variety of uses. Cottonseed oil, palm oil and phulwara butter have been reduced to alcohols. Cetyl alcohol has been prepared in pure form by fractional distillation. Lauryl alcohol has been prepared similarly from trilaurin obtained from pisa seed fat. The work will be continued in co-operation with the Chemical Engineering Division.

XVII. CHEMICALS FROM CASTOR OIL

Laboratory scale experiments have been carried out on the cracking of castor oil to undecylenic acid and heptaldehyde and on the alkaline degradation of castor oil to sebacic acid and 2-octanol. The object is to collect data for pilot plant work in collaboration with the Chemical Engineering Division.

XVIII. MODIFICATION OF NICKEL CATALYST FOR THE HYDROGENATION OF OILS

This scheme, sponsored by the Bombay state Industrial Research Committee, was terminated on 30.11.57.

Both the methods of continuous washing for precipitation of basic nickel carbonate and electrolytic

precipitation of nickel hydroxide were found to be satisfactory for the preparation of nickel catalyst by the wet-reduction process. Chromium, silver and molybdenum were found to be satisfactory promoters for the nickel catalyst when co-precipitated.

XIX. UTILISATION OF NON-EDIBLE VEGETABLE OILS AS LUBRICANTS

Several synthetic anti-oxidants were found to be satisfactory stabilizers for refined karanja, mahua and taramira oils. Engine tests were carried out on five blends of nim and castor oils and two blends of karanja and castor oils. Of these the best results were obtained with 1:1 blend of castor oil and alkali-refined nim oil containing α-naphthylamine (1%) and tricresyl phosphate(2%). Results of a 480-hour engine test with this blend compared favourably with those of standard mineral lubricating oils, except for slightly higher values of sludge. The scheme, which was financed by the ICOC, was terminated on 28-2-58.

XX. WORK IN THE DIRECTOR'S LABORATORY (1-10-57 to 31-3-58).

(a) The chemistry of commercial dyes

Mayvat Brilliant Red AF is a halogenated 3:4:9:10-dibenzpyrene-5:8-quinone like Indanthrene Scarlet 4G. These two dyes are suitable raw materials for the preparation of 3:4:9:10-dibenzpyrene, which is a potent carcinogen.

Work on the constitution of Indanthrene Khaki GG, nitrated dibenzanthrone, and certain other anthraquinonoid vat dyes is in progress.

(b) The chemistry of natural colouring matters

Work on the constitution of morellin has been continued and further evidence has been obtained in support of the structural type proposed earlier. Work on the chemistry of mangostin has been continued. Under the auspices of the Indian Lac Cess Committee work has been undertaken on the chemistry of lac dye. A homogeneous crystalline compound has been isolated and both degradative and synthetic approaches are being made for determining its constitution. The synthesis of certain naturally occurring flavones, isoflavones and anthraquinones, some of which have interest because of their physiological properties, is in progress.

XX. MICROANALYSIS

The number of compounds analysed was 1365, of which 477 were for other institutions.

ESSENTIAL OILS

I. SYNTHETIC PERFUMERY MATERIALS

(a) Macrocyclic compounds

i. Pilot plant project on the synthesis of civetone based on oleic acid is in progress. Nearly 33 lbs. of commercial oleic acid, which should lead to 5 lbs. of pure cis-civetone, has been processed. Reduction of the acyloin with $LiAlH_4$ has shown promise. In this reaction nonoic aldehyde is obtained as a valuable by-product.

ii. In another route, mainly for the preparation of dihydrocivetone, 14 kg. of kamala oil has been processed

acid which was subjected to the Barbier-Wieland degradation to yield about 3.5 kg. of pentadecane-1:15-dicarboxylic acid suitable for conversion to dihydrocivetone. Benzophenone and 1:1-diphenylethylene are obtained as useful by-products in this reaction.

iii. About 14 kgs. of erucic acid have been hydroxylated to 9:10 dihydroxybehenic acid which is being processed for conversion to exaltone and exaltolide. In this reaction also nonoic-aldehyde is obtained as a by-product.

iv. Aleuritic acid derived from shellac has been used as a starting material for the synthesis of macrocyclic compounds. By a series of reactions aleuretic acid has been converted to C_{15}, C_{16} and C_{17} 1-ω-dicarboxylic acid with or without unsaturation in the 9:10 position in the fatty acid chain, and to ω-hydroxy-hexadecenoic acid and the corresponding saturated acid. Synthesis of ω-hydroxypentadecanoic acid and a suitable acid for the synthesis of ambrettolide are also under investigation. This investigation should lead to the synthesis of most of the well-known macrocyclic perfumery compounds, barring muscone. As yields in all the stages are excellent, larger scale preparation of some of the intermediates will be undertaken in the near future.

vi. In another similar reaction, the acetylenic compound, 10:11-undecenolic acid, in the form of its ester has been condensed with a series of alkyl halides to give long chain acetylenic acids which on hydrogenation gave the saturated C_{16}, C_{17} and C_{18} acids. These are model experiments for the ultimate synthesis of long-chain

vi. A modified method has been established for the synthesis of azelaic acid and brassilic acid in high yields using dihydroxystearic acid, dihydroxybehenic acid and aleuritic acid as starting materials. These dicarboxylic acids are useful intermediates for the synthesis of macrocyclic compounds.

(b) Dihydrojasmone

A four-step synthesis based on octanone-2 has been established for the synthesis of dihydrojasmone. The yields in all the stages are about 90%, the overall yield being about 66%. This method should supersede other methods now used for the synthesis of this compound, which is a suitable substitute for jasmone, the main odourous constituent of jasmine concrete.

The earlier method for the synthesis of dihydrojasmone using acetone dicarboxylic ester may prove useful for the synthesis of jasmone.

(c) Peach-aldehyde (γ-undecalactone)

A method of preparation for peach-aldehyde or γ-undecalactone from undecylenic acid has been standardized on a kg. scale, the yields being 55-60%. Perchloric acid in catalytic quantities has been found to have a small but significant effect on lactonization. Treatment of peach-aldehyde with polyphosphoric acid gave dihydro-isojasmone in about 50% yield. This compound could also be obtained directly from undecylenic acid by treatment with the same reagent, the yield being about 33%.

II. ESSENTIAL OILS

(a) Costus root oil

The method for the extraction of costus root oil developed by us has been thoroughly standardized. Pilot plant experiments on the extraction of more than one ton of the roots has started. This should lead to the isolation of about 150 lbs. of this valuable oil, and 30 lbs. have already been collected. The method of extraction has been covered by patents in U.K., U.S.A., France, Switzerland, Holland and Germany.

The constituents of costus root oil are also being examined. One of the costituents is a solid crystalline lactone, m.p.108°. Considerable progress has been made on the elucidation of its structure. The hydrocarbon components, α-and β-costene have been separated by distillation and are being further purified by chromatography.

(b) Agarwood oil

Four maunds of the wood supplied by the Govt. of Assam have been extracted by petroleum ether and about 600 g. of the oil concrete has been isolated. This has been separated by high vacuum distillation into volatile and non-volatile parts. Components of the non-volatile fraction have been separated by chromatography on activated alumina into about 100 fractions from which 16 main fractions have been isolated. From U.V. and I.R. absorption of the original oil one of the compounds appears to be an $\alpha\beta$-unsaturated ketone.

(c) Vetiver oil

Vetiver oil is an important article of commerce, and oil of Indian origin has not been systematically examined so far. Four samples of the oil have been collected from different areas in the North and one sample from the South. After total distillation in high vacuum, the components of two of the oils have been separated by fractional distillation and the hydrocarbon portions further purified by column chromatography. Some of these appear to be new compounds.

(d) Wild ginger oil

About 20 lbs. of the oil were obtained from Kozhikode and about 4 maunds of the roots obtained from another source were extracted. The oil has been separated into its components, the more important of which are the crystalline ketone zerumbone, a mixture of humulenic hydrocarbons and an alcohol, possibly belonging to the same group. Zerumbone has been converted to tetrahydro-zerumbone, its oxime and semicarbazone, and reduced by the Wolff-Kishner method to tetrahydrohumulene. Crystalline hexahydrozerumbone has been reduced through the Wolff-Kishner reaction and by desulphurization of the thioketal obtained from the ketone and ethane dithiol. I.R. examination of these products show a ring system similar to humulane. Ozonisation followed by oxidation with permanganate and hypobromite gave a C_{13} dicarboxylic acid, thus confirming the presence of a large ring system in zerumbone.

III. SPECTROPHOTOMETRIC EVALUATION OF ESSENTIAL OILS

A method has now been established for the quantative

citral-content through U.V. absorption at 238 mu. This method, unlike the chemical methods, gives the citral content and not the total carbonyl content.

PHYSICAL CHEMISTRY

I. D.D.T.

Simple and inexpensive formulations for water-dispersible DDT pastes yielding stable suspensions in water nave been reported earlier. Work on water-dispersible DDT powders which have some advantages over pastes has now been undertaken. A new high speed spinning top unit (1000-2000 rps) for the spray atomisation of molten DDT with suitable wetting and dispersing agents was designed and fabricated. As molten DDT supercools before crystallising, powders of desired fineness cannot be obtained unless nucleating agents are added. A study of the rate of crystallisation of molten DDT in the presence of a number of possible effective nucleants was made. Stearic acid, stearamide and benzamide gave promising results.

II. SURFACE CHEMISTRY

(a) Prevention of water evaporation

The prevention of losses caused by the evaporation of water from reservoirs, lakes, etc., assumes great significance for arid regions. Australian workers have had some success in retarding the evaporation of water by spreading films of long chain fatty alcohols. The object of our new project is to study the phenomenon under conditions prevailing in India. A vertical pull

balance for measuring film pressures and a rectangular trough and horizontal pull film pressure balance for measuring the specific water evaporation resistance have been designed. Experimental work is in progress.

(b) Electro-deposition and vapour phase deposition

The effect of additives on the electroplating of metals to yield smooth and bright surfaces is of considerable interest to the electroplating industry. A study of the effect of hydrogen peroxide and sodium fluorite on the bright plating of nickel from a sulphate-boric acid bath, and of thiourea and carbon disulphide on the bright plating of silver from cyanide baths has been completed.

Studies on metal deposition have been extended to include vapour phase deposition of metals and their compounds. Molybdenum deposited from the vapour phase has been found to have both face-centred cubic and close-packed hexagonal structures. Theoretical calculations have shown that single crystals of zinc and cadmium could be grown on plastic surfaces if they could be evaporated into conical cavities of semi-vertical angle less than 10°. Experiments showed that to obtain these crystals the rate of metal evaporation and the precision of the cavity tip have to be critical.

(c) Corrosion and its prevention

A study of the kinetics of corrosion of metals and alloys in various dry and wet environments, and in the presence of protective films, has been initiated. Suitable micro-balances for studies on dry corrosion

of crystal orientation of electro-deposited nickel on the corrosion of mild steel has been made. It was found that (210) oriented nickel coating gave the best protection against corrosion.

The nature and stability of oxide films formed on Fe, Co, Ni and Mn under different conditions of oxygen pressure and temperature have been studied.

III. SOLID STATE CHEMISTRY

An important application of oxidic semi-conductors related to 'thermistors' having high temperature coefficient of resistance. These thermistors are used as temperature measuring and controlling devices and in many electronic circuits. A series of manganite spinels and their solid solutions were studied for their electrical conductivity at various temperatures. The characteristics of these materials as influenced by temperature and the nature of the manganite have been obtained so that any given set of requirements can be fulfilled by suitable formulations.

In addition to the structural studies on manganite spinels described in the previous report it has now been established that the entropy of transformation from tetragonal to cubic spinel as determined by differential thermal analysis agrees with that calculated on considerations of statistical thermodynamics.

A detailed infrared spectroscopic study of zinc manganite, cadmium indate and a number of titanates has been made.

Solid state diffusion studies using radioactive isotopes were continued.

IV. COLLOID CHEMICAL AND SOLUTION PROPERTIES

A study of the kinetics of degradation of rubber by various agencies such as heat, light, ultrasonic radiation, neutron source and γ rays has been initiated. A sample of rubber suitable for degradation studies and having a molecular weight of 300,000 in cyclohexanone has been prepared.

As part of a project, recently initiated, on the preparation of rayon grade pulp, suitable procedures for an ultracentrifugal molecular weight determination of polydispersed materials such as cellulose are being investigated.

Ultracentrifugal studies of polymethyl methacrylate fractions were made in acetone with a view to correlate them with viscosity and light scattering data.

A study of the interaction of metallic ions with proteins and model ligands was continued.

Radioactive tracers were employed to study the effects of temperature, concentration, viscosity, and dielectric constant on the diffusion of trivalent ions in solution.

V. MOLECULAR STRUCTURE STUDIES

An infrared spectroscopic method for the estimation of stigmasterol in a mixture of sterols has been standardised. Preliminary experiments have indicated that benzene hexachloride formed under the influence of radiations from Ra-Be neutron source has a higher content of the important γ isomer. A detailed structural investigation of n-alkyl malonic acids and their diethyl esters is in progress.

Theoretical studies in structural organic chemistry

VI. COLLABORATIVE WORK AND SERVICES RENDERED

In addition to a large number of repair and fabrication jobs done by the Instrumentation Section, the following work was carried out for the Laboratory and outside agencies : (1) A fully automatic polarograph and a spectropolarimeter incorporating a photomultiplier tube have been designed and assembled. (2) A double-beam attachment to the Grubb-Parsons' infrared spectroscope was set up. (3) A bridge for measuring the thermal conductivity of materials has been set up and is in use for testing thermally conducting rubber being developed in the Plastics & Polymers Division. (4) Assay of labelled compounds for their C-14 content was continued (for Biochemistry Division). (5) Studies on kinetics of corrosion of nickel and monel metals were made in dry Hydrochloric acid (Chlorine and their mixtures at 250° (for Chemical Engineering Division) (6) A comparative study of 15 rubber solutions was made for their electrical conductivity (for P&P Division). (7) 234 compounds from the Laboratory and outside organisations were analysed for their molecular structure and functional groups by infrared spectroscopy. (8) Diagnostic studies on anaemia were made by vitamin B-12 labelled with Co-58. A large number of patients and volunteers ware given test doses and the distribution and assimilation of vitamin B-12 ascertained in collaboration with the Military Hospital in Poona. (9) A number of samples of Jowar seeds were subjected to different levels of radiation from 100 mc Ra-Be neutron source (for the Agricultural College). (10) Front surface aluminizing of mirrors and buses (for Department of Chemistry, Poona University and Institute of

techniques, such as X-ray diffraction and differential thermal analysis, connected with a study of clay minerals (for the Rly. Testing & Research Centre, Lucknow). (12) Setting up and servicing of a high vacuum coating unit (for M/S. Reliable Plastic Industries, Bombay). (13) Repair, realignment and recalibration of Beckman model IR-2 infrared spectroscope (for National Physical Laboratory, New Delhi). (14) Construction of two stabilised power supply units and control panels for high voltage electron diffraction camera (for Atomic Energy Establishment, Bombay). (15) Twenty samples were examined by X-ray diffraction (for Technical Development Military Explosives and Institute of Armament Studies, Kirkee).

PLASTICS & POLYMERS

I. FUNDAMENTAL STUDIES IN HIGH POLYMERS

(a) Polymerisation

i. Low temperature polymerisation of methyl acrylate was undertaken. Since peroxides in the presence of tetriary amines are very effective in initiation of polymerisation at reduced temperatures, an amine peroxide system was employed in the study. Conditions were stantardised for investigation of the kinetics of the reaction in ethyl acetate solution at 35°. The sealed ampoule technique was employed. Preliminary results show a direct variation of the overall rate of polymerisation with the concentration of the amine.

ii. In the studies relating to the role of diradicals in polymerisation, phthaloyl dibenzoyl peroxide was used as initiator. This was prepared in a pure form and used as initiator for polymerisation of methyl

methacrylate at three different temperatures in the range 55 - 70°. A significant result is that diradical propagation is shown to be absent in the system. The results are compatible with the kinetic equations derived for conventional monoradical initiators. A paper comprising these results and discussing the probable mode of deactivation of the diradicals produced has been prepared for publication.

iii. Investigation of vinyl polymerisation initiated by hydrazine hydrate in aqueous solution was undertaken. The free radical nature of the reaction was established first. Evidence hitherto obtained points to an initiation reaction involving hydrazyl radicals. The relationship between the rate of polymerisation on the one hand and the concentration of monomer and initiator and the pH of the system on the other were studied. The role of oxygen in the reaction and the catalysis by trace metal ion (e.g. Cu^{2+}) are being investigated.

(b) Solution properties

Recently there has been interest in the viscosity behaviour of polymer solutions at very high dilutions. Different views have been expressed to explain the observed anomalies in the viscosity behaviour of polystyrene, polyvinyl chloride, polyvinyl acetate, etc., at very low concentrations. On the basis of the work carried out in this Laboratory on the dilute solution viscosity of sol rubber solutions in benzene and n-hexane, it was concluded that since the viscosity concentration curve is very much influenced by shaking the solutions prior to viscosity measurements, disentanglement and extension of the polymer

chains at high dilutions is responsible for the observed anomalies in viscosity at high dilutions. This work has now been extended to solutions of fractionated polystyrene in benzene (a good solvent) and methyl ethyl ketone (a poor solvent) at two temperatures. The results indicate that shaking the solutions before viscosity measurements gives a linear viscosity-concentration relation in the case of benzene solutions at 30° and 40° ; and anomaly reappears if the period of shaking is increased. For M.E.K. solutions there has been an anomalous increase at 30°, the departure from linearity increasing with increasing period of shaking and an amomalous decrease at 40° which vanishes as the period of shaking is increased. Quantitative estimation of the adsorption of polymer on the walls of the capillary of the viscometer, which could be an alternative explanation for the observed anomalies, was attempted interferometrically and had to be abandoned due to poor reproducibility.

In case of polyvinyl acetate (linear) in toluene it was shown that adsorption alone cannot quantitatively explain the anomalous viscosity behaviour at high dilutions.

II. POLYSTYRENE

In the polymerisation of styrene by suspension most of the conditions for obtaining a general purpose polystyrene moulding powder have been established. These are : catalyst concentration, temperature, proportion of suspending agents,and monomer/water ratio. A three-phase suspension technique using oxidised sugarcane wax as auxiliary agent in combination with inorganic precipitates such as calcium phosphate has been developed which permits

high monomer/water ratios. A few samples prepared on a 5-liter bench-scale unit have been sent to an outside party for evaluation. The molecular weight distribution and mechanical and moulding properties of our product are under study.

III. ION-EXCHANGE

(a) Preparation of cation-exchange resin from cashew-nut shell liquid (CNSL)

The stock position of the resin prepared on the bench-scale unit is as follows :

i.	Normal quality with exchange capacity between 2.0 and 2.2 meq/gram. ...	1,054 lbs.
ii.	Lower capacity resin obtained dufing standardisation experiments. Capacity between 1.5 and 2.0 meq/gram. ...	506 lbs.
	TOTAL	1,560 lbs.

The sulphonation has been carried out in a lead-lined kettle fabricated in the NCL workshop. For the first stage polymerisation of CNSL a kettle capable of handling 2½ lbs. of CNSL was initially used. Based on the data gathered the Chemical Engineering Division prepared a blue print for a large scale polymerisation kettle and quotations were invited. A kettle with a trap door at the bottom, fabricated in the workshop, has been successfully used to handle 20, 30, and 40 lbs. of CNSL per batch. Further trials are under way.

(b) Water softening

A 2.5 cu.ft. unit containing the CNSL cation-exchange resin has been installed near the large boiler. Three storage tanks of 300 gallons capacity each were

installed to collect the softened water for feeding the boiler. The experiment was conducted for a period of four months and it was found that no scales had formed in the boiler which had been cleaned prior to the experiments. The water softening unit was operated for studying various factors such as concentration of regenerant, rate of regeneration, and rate of flow. The three-column bench unit was operated to collect data for determining the concentration range of regenerant to be used.

(c) Electrodialysis

Preliminary work was conducted with a solution containing a mixture of calcium and sodium chlorides in different proportions. The progress of salt removal was studied at different flow rates by estimating the total hardness, total solids and chloride contents of the samples.

(d) Studies on the CNSL cation-exchange resin

i. The characterisation studies of the resin were completed and the results have been published.

ii. Titration curve studies of different polymers were completed. The absence of OH activity in the CNSL-HCHO-HCL polymer and cardanol-HCHO-HCL polymer was confirmed. The results have been communicated for publication.

(e) Anion-exchange resins

Preliminary experiments have been undertaken with a view to prepare suitable anion-exchange resins.

IV. RUBBER

(a) Liquid rubber

By the standardised method liquid rubber was prepared and tested for casting printing rollers, and for hard rubber linings and casting. Five rollers were supplied to a local printing press for evaluation and satisfactory results have been reported. Commercial

exploitation of the process is under negotiation with interested parties. The unit for producing liquid rubber in use in the laboratory has been installed in a local rubber factory for evaluation of all the factors involved in large scale production.

(b) Rubber base adhesives

Liquid rubber was treated with reagents like stannous chloride, sulphuric acid, phosphorous oxy- and tri-chlorides at different temperatures; the last two gave excellent adhesives for paper, fabric, aluminium, glass, and wood. The maximum bond strength of 1100 lbs. p.s.i. was obtained in shear on aluminium strips.

(c) Rubber linings

i. Thermal conductive linings

Compositions based on natural and acrylonitrile rubber were studied for preparing thermal conductive rubber. Glass beakers, metal containers and copper coils were covered with these conducting rubbers and the rate of heat transfer through them was determined. An overall coefficient of heat transfer through covered copper coils was found to be one third of that of the bare coils.

ii. Non-conductive linings

Metal trays were lined with compositions formulated for resistance to conc. hydrochloric acid, hypochlorite and citric acid. The resistance to hydrochloric acid has been found to be satisfactory and the other tests are in progress.

(d) Cyclised rubber

The preparation of cyclised rubber was stepped up to 20 lb. batches and conditions for the control of the quality of the product were established. A few master batches containing different proportions of cyclised rubber

(e) Miscellaneous

For preparing fire- and flame-proof rubber, paraffin was chlorinated and a cable coated with it was tested according to ISS-434. The results are encouraging.

Preliminary work has been started for preparing fast curing and high impact ebonite for use as a material of construction in chemical and engineering industries. Curing time of 14 minutes at 350°F and an impact strength of 1.6 ft. lbs. have been obtained.

V. POLYURETHANES

Exploratory experiments on the preparation of polyurethane flexible foams were carried out by reacting polyesters with different diisocyanates. It was observed that the polyesters used should have a M.W. of 6,000 or above to impart flexibility and strength, and toluene diisocyanate (TDI) gave better results than naphthalene or hexamethylene diisocyanates.

Saturated polyesters were prepared from sebacic and adipic acids, diethylene glycol and glycerine. Unsaturated polyesters were also prepared from fumaric and maleic acids and diethylene glycol. It was found that the use of CNSL cation exchange resin in esterification reduced the reaction time from 24 hours to about 2 hours. Foams were then prepared from these polyesters by reacting them with toluene diisocyanate (TDI), water and tertiary amine (N-methyl morpholine). The densities of some of these foams ranged from 4-6 lbs. per cu.ft.

Castor oil was reacted with TDI and the rate of reaction was studied. It was found that within 30 minutes about 70% TDI reacted with castor oil when reacted in 1:1 molar ratio at a temperature 50°. Foams with densities of

5-11 lbs./cu.ft. were prepared from these polymers. High speed mixing gave uniform pore size and smooth texture to the foam. The physical properties of the foams are under investigation.

VI. SURFACE COATINGS AND UREA FORMALDEHYDE RESINS

(a) Fatty acids prepared from 20 lbs. of tobacco seed oil were utilised in preparing modified alkyds for trials by the industry. Alkyds were tested for wrinkle formation and samples of the composition are now being sent to interested parties for trials.

(b) Further quantities of modified urea formaldehyde resins were prepared using fusel oil and amyl alcohol. Textile bobbins were coated with formulations based on these resins and tobacco seed oil modified alkyds. Urea resins have also been sent to an interested party and the report is awaited.

VII. HONEYCOMB STRUCTURES

A few samples of phenol formaldehyde resins using different alkali catalysts were prepared. Solutions (60%) of these resins in acetone and methylated spirit were used for studying the rate of their penetration in kraft paper. Refinements and modifications in the design of the strip glueing machine have been completed.

This project has now been terminated.

VIII. AD HOC PROBLEMS

(a) Rigid filters

Tests on two filters fabricated in the Laboratory were conducted at the Poona Water Works, and the report was satisfactory. Subsequently, 120 feet lengths of 6"-diameter of slotted tubes were covered with rigid filter layers. A special oven and moulds were fabricated for

filters, which are being sent to an interested party for practical tests by installation in a tube well.

(b) Can-sealing composition

Four gallons of the composition were prepared according to the old formulae and sent for trials by the industry. The shortcomings of the product have been overcome and the composition has been improved to suit the requirements of the trade. A further quantity of the modified composition is being prepared for trials.

(c) Moulding composition

Moulding powder based on molasses treated according to Indian Patent No.53,414 were prepared for trial by the industry. It was also found that pretreatment of molasses with 5-10% of CNSL before dehydration improved water resistance of the mouldings. A wood-flour filled general purpose moulding powder was prepared and sent to industry for testing.

Preliminary experiments were carried out to use cashew nut shells in thermosetting type moulding composition.

IX. TECHNICAL AID

Assistance in the form of technical advice, analytical reports or supply of samples was given to Government Departments, firms and private parties on the following problems :

Water softening and treatment of sea water; ion-exchange; bonding rubber to copper; combustion of vulcanised rubber sheets; rubber castings; improvement in the life of rubber soles and heels; gelation of rubber solutions; cement for bonding iron/concrete, bakelite/brass and one plastic to another; luminescent plastics and colouring of plastics; preparation of nylon-like fibres from castor oil; artificial dentures; printing of cellophane capsules;

coatings for bobbins; polyvinyl acetate; acrylic scrap; polyvinyl chloride; polyethylene; suitability of polyethylene containers for medicinal and other purposes; plastics for moulds and castings; plastic wood for artificial limb; polystyrene pearls; sealing materials for BT bottles; resin-impregnated filter papers; textile resins; adhesives; camel back; and paint formulations.

SURVEY & INFORMATION

I. REPORTING ON THE WORK CONDUCTED IN THE NCL

Reports were prepared and supplied as usual to the Secretary, CSIR, and to the Publications Division.

II. COMMERCIAL INFORMATION SERVICE

(a) New surveys regarding prices and availability were completed for the following :

Ascorbic acid, carbon black, selenium, plasma substitutes, synthetic gemstones, diastase, ion-exchange resins, macrocyclic compounds, cashew-nut shell liquid, marsalyl, electrolytic manganese dioxide, cryolite, sorbitol, phenol formaldehyde resins and moulding powder, absolute alcohol and rectified spirit, electro-plating chemicals, ilmenite, zircon, fluorspar.

(b) Survey regarding consumption of the following has been carried out :

Waxes, rubber antioxidants and accelerators, vegetable tallow, mutton tallow, stearine, food anti oxidants, PVC resins and moulding powders.

(c) A card index of names of Indian manufacturers of chemicals has been compiled. Information regarding 417 chemicals has been collected.

(d) Import data regarding chemicals, connected with the projects which are in progress in the Laboratory, were compiled from daily import lists.

(e) Manufacturers of chemicals in India were contacted regarding their technical difficulties.

(f) Information regarding chemicals required by members of the staff of the Laboratory was collected and furnished.

III. TECHNICAL INFORMATION SERVICE

1098 enquiries on technical problems were received and attended to in consultation with other Divisions of the Laboratory.

IV. Coordination of work conducted in other Divisions has been started by way of studying projects; helping in calculation of cost of manufacture in case of the processes developed in the Laboratory; carrying out market survey; and (when required) literature survey in connection with the Research Projects proposed to be taken up in other Divisions.

V. OTHER SERVICES

(a) Photography and drawing section

The Division continued to serve other Divisions by preparing photographs and drawings as required for publications.

(b) Visitors

6265 visitors were shown round the Laboratory during the year.

II. L I B R A R Y

3347 books, 42 patent specifications, 56 microfilms, and 7 Standard Specifications were added during the period.

Current periodicals, numbering 699, were received regularly. The United States Book Exchange supplied several back volumes of periodicals and serials as gifts.

1531 Indian Patents were received in the NCL Library Patent Inspection Centre.

III. WORKSHOP

(a) Scientific apparatus fabricated in the workshop

1. One die for packing depolarizer mixture in dry cells.
2. Two stands for 40 cu.ft. gas cylinders.
3. Two refrigeration units for vitamin C project.
4. One sodium press similar to that of Gallenkamp incorporating some improvements.
5. Necessary modifications and additions in the components of P.V.C. unit.
6. One two-stage sieving machine for P. & P. Division.
7. One 15 cu. ft. capacity refrigeration chamber for Director's Laboratory (Tem. range. 0° to -5°).
8. High voltage electron diffraction camera (Finch Type) for Atomic Energy Establishment.

(b) Total number of jobcards received - 2894.

Total number of jobcards completed - 2862.

IV. PAPERS PUBLISHED AND COMMUNICATED

PAPERS PUBLISHED

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6. Ramachandran, B.V., An improved method for the preparation of L-arginine monohydrochloride, J. sci. industr. Res., 1957, 16C, 196.

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7. Bijawat, H.C., Rates and activation energy for the decomposition of limestone, Chemistry & Industry, March 16, 1957, 331.

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19. Seshadri, K., and Lobo, J., Polytherm of the Quarternary System Sodium Chloride - Sodium Sulphate-Sodium Carbonate - Water, J. sci. industr. Res., 1957, 16B, 12, 531-538.

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20. Ojha, V.N., Sharma, P.G., and Aggarwal, J.S., Modification of kamala seed oil for varnishes and paints, J. sci. industr. Res., 1957, 16A, 213.

21. Gupta, A.S., and Aggarwal, J.S., Esterification of phenols and hexadecamethylene 1:16 - dicarboxylic acid, J. sci. industr. Res., 1957, 16B, 181.

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