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# INORGANIC CHEMISTRY

## IC-I. CHEMISTRY OF RARE METALS

### (1) Studies in the isolation of pure rare earths

*(January 1955 as AEC Scheme; supported by the regular staff since Sept.,1957)

Fundamental studies on the complex-forming property of sodium triphosphate (tripoly) with some rare metals during this year have led to the introduction of a new complexing eluant for the separation of the rare earths. It has proved to be particularly useful in the preparation of pure samaria from a 30 per cent samarium concentrate with 60 per cent recovery in a single pass from a column loaded to 40 per cent of capacity. As is well known, citrate elution is far from satisfactory in such cases. Qualitatively, it may be said that the resolving efficiency of the new eluant is between citric acid and EDTA for the light rare earths. Heavy earths will require further and systematic examination. A satisfactory laboratory method of preparation of sodium triphosphate hexahydrate of good purity from trisodium phosphate of commerce (a product of Indian Rare Earths Ltd.) has been worked out giving a uniform average purity of 95 per cent of the former, the rest being principally pyrophosphate.

The isolation of two 80 per cent concentrates, didymia-samaria and lanthana, from the monazite rare earths mixture by controlled hydrolytic precipitation, and the recovery of 99.9 per cent lanthana from the second were mentioned in last year's Report. The first concentrate (didymia-samaria), which had an average composition $Pr_6O_{11}$ 15, $Nd_2O_3$ 56, $Sm_2O_3$ 9 and $La_2O_3$ 20 per cent on ignition, was processed for separation. Of the several alternative fractional techniques tried, the best was to resolve the quaternary mixture into binary concentrates and then apply different processes for final resolution. Laboratory conditions for resolution of the quaternary mixture have been standardized to yield a 35 per cent samaria- and a 90 per cent neodymia-concentrate, with some recovery of pure praseodymia and lanthana, and the process is being developed for work on a larger scale. For resolution of the samaria-concentrate, the triphosphate method so far appears to be the best compromise between ideal separation and economy of time and material.

The offer made by a firm for exclusive sales agency for the pure rare earths and a few other oxides produced by the Laboratory's processes is being considered in consultation with the Department of Atomic Energy.

### (2) Separation of zirconium from hafnium

(January 1957 as AEC Scheme)

The background of the investigation, the opening up of Indian zircon with alkali, preparation of the iron-free natural mixture of zirconium-hafnium oxychloride octahydrate (Hf/Zr = 3.0 ± 0.15 per cent) and resolution of the natural mixture by frontal separation of a methanolic solution of

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*The date of commencement of each research scheme or project is stated within brackets after the title in this Report.

the hydrate on activated silica gel, was described in earlier Reports. Economic application of the chromatographic technique requires re-usability of the methanol and the gel after a minimum of processing, which was the main problem studied and solved during the year. In view of the possibly greater adaptability of the present process to Indian conditions than those based on the handling of anhydrous chlorides, certain basic data, e.g. yield of pure zirconia (Hf/Zr less than 100 p.p.m.) per pound of gel, fractions of oxide equivalents of pure zirconia, low-hafnia (Hf/Zr about 0.5 per cent) zirconia and hafnia concentrate (Hf/Zr over 20 per cent) were worked out from a number of experiments on a medium scale. The variable quality of silica gel obtained from suppliers has proved to be a source of some trouble, and the possibility of making one of uniform grade from the sodium silicate obtained as a by-product in the earlier stage of the process, is to be examined.

The 20-40 per cent hafnium concentrate recovered from the silica gel columns served as the starting material for the preparation of pure hafnium oxide. The anion-exchange method, first reported from this Laboratory in 1955, was used with slight modifications, increasing the workable load and making the columns practically continuous in operation. The anion was the double fluoride, impregnated on a strong anion exchanger (sulphate form) and eluted with dilute sulphuric acid. The hafnium which ran out first was freed from iron by solvent extraction and finally obtained as the white oxide $HfO_2$.

Some systematic data on solvent extraction were collected on the differential extractability of zirconium and hafnium. Several oxygenated solvents, most of which are produced in the country, were found to extract zirconium and hafnium discriminatively from nitric acid solutions, from a practical view-point some appear to offer possibilities of separation in a multi-stage technique, especially in presence of a salting out agent such as calcium nitrate.

### (3) Separation of niobium from tantalum
(October 1957)

Tantalo-columbites, though reported from over twenty places in India at different times, are scheduled minerals under the Atomic Energy Act, and detailed estimates are not available to the public. As is well known to-day, niobium and high-niobium alloys are important materials for breeder reactors and air-craft jet engines. However, niobium is coexistent with tantalum in all its minerals, to which it is chemically similar to such an extent that a separation between them has been a long-standing chemical problem. Many separational techniques, including the relatively recent ion-exchange and chromatographic procedures, were tried without great success. The solvent extraction technique has recently proved very successful, but only limited information is available in published literature.

With a sample of Indian mineral supplied by the Department of Atomic Energy, a laboratory method of obtaining both the constituents in a highly purified state was worked out. The method has the twofold advantage of working at relatively very low acidities and using a solvent which is produced commercially in the country. A complete flow sheet of the process and working details have been made available to the Department of Atomic Energy, for carrying out comparative studies with certain other methods also under examination by the Department.

## IC-II. PREPARATION OF SPECIAL INORGANIC CHEMICALS (December 1958)

The purpose of this flexible long-term project is to prepare a number of industrially important chemicals which are not being produced in the country and whose preparation involves special manipulative skill. Economic factors are kept in view at all stages of development of the methods of choice. The special chemicals tackled during the year are briefly discussed below :-

### (1) Sodium hydride

This chemical is important in synthetic organic chemistry and is the starting material for making complex boro- and alumino-hydrides. It was prepared by pressure hydrogenation of sodium in high-boiling kerosene. Sodium borohydride was obtained in almost theoretical yield by reacting the hydride with meth,l borate prepared from boric acid and methanol. Attempts are being made to replace the pressure hydrogenation method for sodium hydride by hydrogenation under atmospheric pressure of the highly dispersed molten metal.

### (2) Fluorescent zinc sulphide

Leverenz has stated that there is no effective substitute for personal experience in synthesizing phosphors. The extreme carefulness required during their preparation in order that the beneficial effects of tiny proportions of activators may not be obscured by the presence of unknown contaminants is well known. At the urgent request of a Government Department, the green phosphor was prepared to specification and 10 lb. were supplied. The investigation has also led to a simplification of the method recommended in the literature.

### (3) Oxides for semiconductors

They are required in a state of extra high grade of purity in connection with this Laboratory's thermistor project and other problems of solid state chemistry. Processes are being developed to prepare oxides of the desired purity from the purest salts available in the Indian market. Some of these methods have yielded products whose spectrographic examination shows that their purity is comparable to corresponding grades of products of British manufacture.

### (4) Soda-lime granules for hospitals

A granular product, which has been stated to be at present wholly imported, was examined and prepared at the request of a member of the staff of the American Technical Cooperation Mission operating in India. The laboratory sample was non-deliquescent and showed a $CO_2$ absorption efficiency comparable to "Calona" of British manufacture. The import of this product is not large, but its ready availability in the country at all times is a more important factor.

## (5) Titanium organics

Renewed interest was noticeable during the year in the titanium-incorporated CNSL-formaldehyde insulating varnish which was developed in 1955 (Indian Patent No.55171), including some enquiries from Government Departments. Tests carried out according to B.S. Specification 119-1930 at the Government Test House and other places show a generally acceptable set of properties, but a few properties such as viscosity and ageing characteristics require improvement. Modified samples are under preparation for further tests. A request for purchase of the patent is also pending with the N.R.D.C.

In addition to those mentioned above, a few special products such as activated alumina for liquid air plants, optical glass polishing powders and abrasives are under examination. Among the special chemicals supplied to bonafide consumers in research institutions, mention may be made of 10 lb. of titanous chloride (15 per cent w/w) prepared from chlorinating commercial titania and electro-reducing the titanium tetrachloride in acid solution.

## IC-III. EXPERIMENTS ON INDIAN BARYTES
(April 1959)

Barytes, an essential raw material for the manufacture of barium chemicals, occurs in India in Andhra and Rajasthan, and in smaller amounts in Madhya Pradesh, Kashmir and Bihar. Total reserves in the first two States exceed a million tons, much of which is chemically of fairly good grade. However, large quantities of barium chemicals, including the simple salts, are imported. Only a small fraction of the barytes mined in Andhra, of a pure white grade, finds some market among paint manufacturers; the rest is mainly exported.

On the receipt of some samples from the Government of Andhra Pradesh, a chemical process was developed during the year to convert off-colour barytes to products suitable for incorporation in rubber and as an extender for paints, according to I.S.I. specifications as well as actual trials. The results were made available to the State Government. Secondly, as an alternative to the process of high-temperature reduction of barytes by carbon or water-gas to barium sulphide followed by acid conversion to salts, a process of a single-step reduction-cum-chlorination was studied with two samples from Andhra Pradesh and Rajasthan in the lower temperature range of 500-800$^{o}$ in vertical reactors. Only laboratory-scale experiments have been carried out so far, giving good and reproducible results. A mixture of sulphurous by-products, recovered during the chlorination, is being chemically examined. The chloride is easily obtained pure by extraction and crystallization of the chlorinated mineral, and can be converted with a high degree of conversion efficiency to the nitrate with sodium nitrate or nitric acid. In the laboratory experiments carried out so far, factors such as time, temperature, proportion of reactants, chlorine feed rate, bed dimensions, catalysts, different extractive treatments and methods of purification have been studied.

The Indian mineral celestite (strontium sulphate) is also being examined along similar lines for the preparation of strontium chemicals.

## IC-IV. CATALYTIC OXIDATION OF SULPHUR DIOXIDE TO TRIOXIDE (July 1959)

The commercial process of oxidation of sulphur dioxide to trioxide by air is a heterogenous catalytic reaction that has been extensively studied. There is general agreement on the superiority of vanadium-potash-silica catalysts, now manufactured on a very large scale by a few foreign firms in association with fabricators and suppliers of contact sulphuric acid plants. With Indian plant designers and fabricators entering the field, the production of catalyst of standard performance in the country assumes special importance. A mass of patent literature exists on catalyst manufacturing procedures, but the methods in actual use are still regarded as trade secrets.

At the request of a large manufacturer of contact sulphuric acid, the problem of making a vanadium catalyst of standard quality was undertaken. Industrial samples show that the fresh catalyst is essentially a mixture of $V_2O_5$, $K_2S_2O_7$ and silica, and the spent one a tetroxide of vanadium in place of the pentoxide, with varying water contents. A small fraction of the vanadium in the fresh catalyst supplied by the firm is in the tetravalent stage, but its prior incorporation in the synthetic samples is not found essential, as a little vanadium can be suitably reduced at the activation stage to provide a defect structure of the oxide lattice as good as any in inducing surface adsorption followed by chemical oxidation.

In course of the laboratory investigations, a few synthetic samples have been prepared from sodium silicate, ammonium vanadate and potassium bisulphate. Reich tests show near-theoretical conversions of a 7.5 per cent v/v $SO_2$-air mixture at $450^\circ \pm 10^\circ$ with some of them at low and moderate space-velocities under equilibrium (isothermal) conditions. These samples are now being tested under non-equilibrium conditions. The activity of the pellets has been found to remain unchanged after batch runs involving alternate heating and cooling, but their crushing strength is not yet up to standard. The possibilities of running small pilot plant trials with the Laboratory's samples at a neighbouring factory are being examined.

## IC-V. ANALYTICAL RESEARCH & SERVICE

This is another permanent project of the Inorganic Chemistry Division with a flexible programme, which is adjusted to some extent to the needs of other projects of the preparative type in the Laboratory. This year the principal analytical service rendered was on emission spectrography, and analytical research pursued was on the polarographic study of complex formation. The service work was mostly in the nature of control analysis, e.g. of zirconium, hafnium, niobium and tantalum in fractions collected in new processes under development, but sundry samples, e.g. of kiln dust and fly ash from cement factories (for lithium) and an iron ore sent by a Government Department (for vanadium), were also analysed by the spectrograph and the flame photometer. The basic sensitivities of hafnium lines in the ultraviolet is being measured in a few matrices such as graphite, zirconium dioxide and silica. Absolute sensitivities of even many strong hafnium lines in the ultraviolet region are not known.

A polarographic study of complex formation of sodium triphosphate (tripoly) with a number of metals having different stable valency states has been undertaken in view of the recent interest developing in polyphosphate complexes of heavy metals, and some interesting observations have already been made, apart from the use of sodium triphosphate in the separation of some rare earths reported here under another project. For a given metal, there is an unmistakable similarity between the triphosphate and pyrophosphate polarograms, but the half-wave potential value is generally indicative of greater stability of the triphosphate complex. Reductions are generally associated with an overpotential indicated by the irreversibility of the waves. One peculiarity observed is that in presence of surface-active agents, e.g. gelatine and camphor, which are adsorbed strongly on the d.m.e., the polarograms are distorted and even totally suppressed, exceptions encountered so far being $Ag^+$ and $Tl^+$. The reason for the absence of wave-maxima, in cases where no surface-active agents have apparently been added, may lie in the surface-active nature of sodium triphosphate itself. Possible mechanisms of reduction of the complexes at d.m.e. are being considered.

## PROJECTS TERMINATED OR CONCLUDED

### (1) Synthetic cryolite

A full report on the laboratory investigations, carried out till April 1959, was prepared and submitted to the Executive Council in August 1959.

### (2) Titanium dioxide from bauxite sludge

A full report of work done up to August 1959 is now ready for submission to the Executive Council.

### (3) Phosphatic compounds

The work was not pursued further for reasons already explained in last year's report. The method developed for sodium tripolyphosphate is being regularly used for making the pure chemical and using it for the separation of rare earths.

# PHYSICAL CHEMISTRY

## PC-I. SURFACE CHEMISTRY

### (1) Suppression of evaporation of water by surface films

(1958)

The suppression of evaporation of water from lakes and reservoirs is a dominant problem especially in arid regions. The use of monomolecular films of cetyl alcohol on water surface has been reported to effect significant reduction in the evaporation of water. However, cetyl alcohol has not been found to be quite satisfactory under Indian conditions. In order to find substances superior to cetyl alcohol as a water evaporation retardant, a few long-chain compounds such as alcohols, esters and ethers have been prepared in a very pure state. Four evaporimeter pans of 4 ft. diameter were set up in the NCL garden for carrying out evaporation suppression experiments under semi-field conditions. A few new compositions have been discovered which are found to give a reduction in evaporation of about 60-90 per cent under laboratory conditions and 50-80 per cent under semi-field conditions as compared to cetyl alcohol giving a reduction of 50-60 per cent in the laboratory and 30-40 per cent under the field conditions.

### (2) Surface-active agents

(1958)

This project was initiated with a view to preparing surface-active agents from indigenous raw materials and studying their fundamental properties. A number of sulfonated derivatives prepared from cashew-nut shell liquid in the Organic Chemistry Division were tested for wetting, foaming and detergent properties. A few of these were found to be efficient foaming and wetting agents and detergents.

## PC-II. SOLID STATE CHEMISTRY

### (1) Thermistors

(1958)

In response to several enquiries thermistors of bead, rod and pellet types of various specifications were prepared and supplied.

### (2) Ferromagnetic materials

(1958

Studies on the synthesis and properties of hard ferrites suitable for sintered oxide permanent magnets are in progress. The variation of induction with applied magnetic field has been studied for a number of phases, isomorphous with hexagonal barium ferrite. The effect of chemical composition on the coercivity and remanance is being investigated.

### (3) Ferroelectricity
(1957)

A study of the ferroelectric properties of the many new phases crystallizing in the pervoskite or lead niobate structure has been carried out. The data have led to a correlation between the variation of dielectric constant and the composition of the various pervoskites.

### (4) Crystal rectifiers and transistors
(1930 )

Using germanium and silicon, work has been initiated to prepare crystal rectifiers and transistors.

### (5) Electroluminescence
(1953)

Methods of preparing phosphors where the concentration of ZnO and ZnS can be controlled have been standardized. A photomultiplier spectroscope set up for the examination of the emission curves of various phosphors has been completed. A thermogravimetric study of the ratio of oxidation of $\alpha$ and $\beta$-ZnS was carried out.

### (6) Thermoelectricity
(1953)

Studies on Peltier cooling were made using various couples made of PbS, PbTe, Te and ZnSb. A thermoelectric generator utilizing the cooling by evaporation of water was tried under various conditions.

### (7) Crystal structure
(1959)

The unit cell dimensions and space groups of morellin, its p-bromobenzenesulphonyl ester, $\beta$-alanine and sodium pyruvate have been determined. The Patterson projections along two axes have been obtained for the first two compounds.

### (8) Corrosion
(1959)

The project was initiated with a view to studying the high temperature oxidation of the metals and alloys which find use in atomic reactor technology. A Gulbransen type quartz microbalance and a differential manometer system have been constructed and are being calibrated.

### (9) Solid state and molecular theory
(1957)

A general theory of super-exchange interaction mechanism has been developed; perturbation calculations on the super-exchange interactions in the magnetic compounds with zinc blende structure have been completed. A theory of the configurational instability of the octahedral systems in degenerate states was formulated which takes into account both the covalency and Jahn-Teller effects.

## PC-III. CATALYSIS

The construction of the BET apparatus for surface area measurements and pore size determination has been completed and its calibration is being undertaken. The construction of low and high temperature calorimeters for the determination of the heats of adsorption and the heat capacity is in progress.

The vapour phase oxidation of $\Delta^3$-carene was studied with a number of catalysts. At temperatures between 360-450° no oxidation took place, p- and m-cymenes were found to be the major reaction products, and were produced in almost equal quantities. The dehydrogenation of Indian turpentine oil was carried out using chromia-alumina catalysts. An analysis of the product by infra-red spectroscopy showed that m- and p-cymenes were the major constituents of all the fractions boiling above 160°. The fraction of m-cymene in in the catalysate varies from 33 to 45 per cent of total cymene, the yield of which is nearly 75 per cent.

A method has been worked out for the isolation of nickel in a pure form from the spent catalyst left after commercial fatty oil hydrogenation. This is being converted into a compound suitable and economical for the same catalytic reaction.

## PC-IV. COLLOID CHEMICAL AND SOLUTION PROPERTIES
(1959)

### (1) Rayon grade pulp project

With a view to determining the supermolecular structure and molecular polydispersity the following were carried out : (a) Fifteen litres of the solvent zinc ethylenediamine (Zn-en) were prepared. A study on binding of this solvent with cellulose revealed that two zinc atoms are bound to one anhydroglucose unit, (b) The crystallinity as determined by Herman's X-ray method lies in the range 0.58 to 0.68 for the imported as well as indigenous pulps, (c) The use of the phase contrast projection microscope showed that the diameter of cross-section in foreign pulps is greater than in the indigenous ones, (d) Swelling in 5 per cent sodium hydroxide solution and Zn-en was studied. Swelling is more uniform in foreign pulps, (e) The intrinsic viscosity $[\eta]$ of each sample was determined at 25°. The values lie between 2.2 to 3.0 decilitres per gram. None of the samples showed non-Newtonian behaviour in the shear rate range 20-100 secs. The temperature dependence of $[\eta]$ shows a slight variation in Huggin's constant, an interesting indication being that this variation is more in the case of less suitable pulps, (f) The preparation of chlorine-free Zn-en solvent has been successfully made by taking ZnO in place of $ZnCl_2$ as the starting material. Fifteen litres of this solvent have also been prepared.

### (2) Kinetics of degradation of rubber
(1958)

Molecular weights of rubber in solutions in cyclohexane and decalin were obtained at different temperatures from the light scattering data.

(3) Light scattering by thin polymer films under strain (1968)

Expressions for the scattering cross-section of anisotropic optical inhomogeneity in thin films under homogeneous one dimensional strain were generalized for a Raleigh scatterer of any degree of strain. The work on two dimensional homogeneous strain has also been completed.

(4) A study of the sedimentation behaviour of $\alpha$-chymotrypsin in phosphate buffer solutions of pH 6.9 ($\mu$=1.0) and 7.3 ($\mu$=0.05) showed that ionic strength greatly influences the degree of polymerization. Similar preliminary study of Indian silk fibroin (mulberry) in lithium thiocyanate solution suggests that the degree of association of the protein molecule in solution is influenced by the concentration of the salt.

The interaction of imidazole with cobalt, cadmium, zinc and nickel has been studied by potentiometeric, polarographic and spectrophotometric methods.

## PC-V. INSTRUMENTATION

The following major fabrication jobs were completed : A number of thyratron relay units; focussing device for an ultra-centrifuge; mechanical parts for crystal pulling furnace; thermistor radio-sonde transmitter; stabilized rectifier power unit for NMR work; a photoelectric diffuse reflectometer for measurement of the washing efficiency of detergents; a signal generator with frequency range from 100 KC to 1 MC for testing resonance and anti-resonance of piezo-electric crystals; 1500 volt continuously variable D.C. power supply. In addition a number of developmental jobs was undertaken.

## PC-VI. USE OF RADIOACTIVE ISOTOPES FOR MEDICAL RESEARCH

(1) As part of a programme to study the problems connected with Kysanur (Mysore State) forest disease virus investigations in collaboration with the Virus Research Institute, Poona, were carried out on monkeys, to determine the shortening of the life of red blood cells in the presence of the virus. Radioactive Chromium-51 was used for this work.

(2) In continuation of the work on the use of radioactive iodine - 131 for diagnosis of thyroid disorders a number of patients from the Military Hospital, Poona, were examined for sites of malignant growth.

# ORGANIC CHEMISTRY

## OC-I. ORGANIC CHEMICALS INCLUDING SYNTHETIC DRUGS

### (1) Synthetic drugs

Earlier work in the direction of establishing suitable procedures for the preparation of some essential and expensive drugs was continued.

(a) Pyridoxine hydrochloride (vitamin $B_6$) (1958) - After successfully completing the laboratory investigations for the synthesis of vitamin $B_6$, pilot plant investigations were carried out with a view to producing one pound lots of vitamin $B_6$ for each charge. Several of the intermediates in the synthesis of vitamin $B_6$ such as 2-methyl-4-ethoxymethyl-5-cyano-6-pyridone and 2-methyl-3-nitro-4-ethoxymethyl-5-cyano-6-chloropyridone were prepared on 700 g. scale in the laboratory.

The regular pilot experiments, aimed at collecting the process and engineering data useful for the designing of a commercial unit, were started in August, 1959. Out of the ten steps involved in the synthesis, the first five steps have been successfully completed. Development work for these steps and the remaining steps were carried out in the laboratory. Yields obtained in the laboratory in each step were equalled or bettered on the pilot plant scale.

Work on the remaining five steps in the synthesis of vitamin $B_6$ is in progress.

(b) Theophylline (1959) - Attempts were made to prepare theophylline by several routes described in scientific and patent literature. Several difficulties were encountered. Ultimately, after much experimentation, a satisfactory process giving good yields at various stages has been developed on the laboratory scale. Further attempts to improve the process are in progress.

(c) Anticoagulants (1958) - 4-Hydroxycoumarin, a key intermediate in the synthesis of anticoagulants such as sodium-warfarin (coumadin), was prepared on a fairly large scale (0.25 to 0.5 kg.) according to the method developed at the NCL (Ind. Pat. No. 62890). Yields of about 64 per cent of 4-hydroxycoumarin have been obtained.

After trying several methods of preparing sodium-warfarin, a satisfactory and simple method for its preparation has been worked out; 400 g. of sodium-warfarin of pharmaceutical grade have been supplied to a leading pharmaceutical firm in Bombay.

### (2) Industrial chemicals

(a) N-Methyltaurine (1959) - After successful conclusion of the laboratory investigation for the production of N-methyltaurine in 90-95 per cent yields from aq. ethylene chlorohydrin, sodium sulphite and methylamine, a few large scale experiments (2 lb. of pure anhydrous N-methyltaurine at a time) were carried out to confirm the optimum conditions established for the procedure. Subsequently a patent application (Ind. Pat. No.70319) has been filed.

(b) Chloral hydrate (1959) - At the request of Hindustan Insecticides, Delhi, the problem of developing a suitable procedure for the preparation of B.P. grade chloral hydrate from the tech. chloral supplied by them was taken up. A simple method has been developed. The residual mother liquor, useless for further recovery of chloral hydrate, has now been put to use for the production of chloroform and sodium formate as useful by-products.

(c) Methylamines (1959) - Laboratory investigations for the preparation of methylamine by catalytic vapor phase condensation of methanol and ammonia are nearing completion. Optimum conditions regarding temperature, catalyst, ratio of reactants, etc., have now been standardized so that nearly 80-90 per cent utilization of the methanol is accomplished. A satisfactory method for the determination of each of the components (mono-, di- and trimethylamines, ammonia, methanol and water) present in the reaction mixture has been worked out.

(d) Trichlorobenzenes (1959) - The chlorination of mixed o- and p-dichlorobenzenes (by-product of Hindustan Insecticides, Delhi) to trichlorobenzenes, useful as solvents, is being studied.

## OC-II. WAXES

### (1) Modification of sugar-cane wax (1958)

The pilot plant work on the modified sugar-cane wax was concluded in December 1959. Large quantities of amide wax, ester wax and oxidized wax were supplied to various firms for testing.

### (2) Sisal wax (1959)

The extraction has been carried out on a pilot plant scale by two different methods, and the latter method has been found to be more satisfactory. Samples of sisal wax have been sent to various firms for testing. The pilot plant work was concluded in February, 1960, but work on the composition of the sisal wax is in progress.

## OC-III. CINCHONA ALKALOIDS
(1959)

### (1) Conversion of quinine to quinidine

Known methods and their modifications have been studied. By suitable oxidation and reduction a conversion of 50-55 per cent is obtainable, and the economics are being studied.

(2) Cinchona febrifuge

A method has been developed for recovering quinine (7 per cent) and quinidine (4-5 per cent) from cinchona febrifuge.

(3) Exploratory experiments have been undertaken on the preparation of new chemotherapeutic agents from quinine.

### OC-IV. BOROHYDRIDES IN SYNTHETIC ORGANIC CHEMISTRY (1959)

A new synthetic route to the naturally occurring anthraquinone carbinols has been developed by the selective reduction of anthraquinone carboxylic acids by diborane. A new method of reducing anthraquinone derivatives to the corresponding anthracenes has also been developed. Attempts are being made to examine if the reduction of CO to $CH_2$ observed in xanthones, flavones, chromones and quinones can generally be extended to other keto groups.

The effect of the addition of metal halides to sodium borohydride and investigation of the reducing properties of the resulting complex borohydride was continued. Complex borohydrides formed by the addition of halides of cobalt, manganese, iron, zirconium and molybdenum and their reducing action have been studied.

### OC-V. CONSTITUTION OF NIMBIN (1958)

A process has been established for obtaining nimbin, a crystalline product obtained from the bitter principles of neem oil, in good yields by chromatographic methods. Considerable progress has been made, with the result that a working formula for nimbin can be postulated. It has been established that nimbin is a pentacyclic compound having a $\beta$-substituted furan, a cyclic ether, an acetate, a ketone, and two carbomethoxy groups, one of which is probably unsaturated.

### OC-VI. UTILIZATION OF THE PHENOLIC COMPONENTS OF CASHEW-NUT SHELL LIQUID (1959)

(1) Surfactants - Surfactants of both the ionic and nonionic types have been prepared and examined.

(2) Pesticides - Anacardol and tetrahydroanacardol were chlorinated to various extents. The products have insecticidal properties. Their germicidal and antiseptic properties are being determined.

(3) Solvents - Ethers were prepared with a view to developing some thermally stable solvents and heat exchange media.

(4) Phenoxyacetic acids of anacardol, tetrahydroanacardol and their chloro derivatives were prepared. They are being tested for their herbicidal and other properties.

## OC-VII. UTILIZATION OF INEDIBLE OILS
(1950)

(1) Kamala seed oil
(1958)

Studies on the keeping qualities of kamala seed oil and kamlolenic acid were continued.

(2) Fatty alcohols from cottonseed oil
(1959)

Ethyl esters of cotton seed oil were prepared and subjected to hydrogenolysis. Satisfactory conversion of esters to alcohols has been observed in the few trial runs. Procedures for the separation of fatty alcohols from unconverted esters and the separation of saturated and unsaturated fatty compounds are being worked out.

(3) Chemicals from castor oil
(1958)

(a) Undecylenic acid and heptaldehyde - A new stainless steel reactor was set up for the cracking of castor oil. Good yields could be obtained by the careful control of temperature, vacuum and rate of flow, but these were found difficult to maintain except in the case of a few runs. However, irrespective of the yield, the analysis of the various fractions, obtained from experiment to experiment, showed them to be similar in nature. The 'lighter fraction' obtained during distillation of cracked products was catalytically hydrogenated to give c.p. grade stearic acid. Work on the condensation products of the aldehyde and amines was continued. Two large samples have been prepared and sent for testing.

(b) Sebacic acid and 2-octanol - A procedure has been standardized which gives 62 per cent conversion of the ricinoleic acid into the desired products. Five batches of castor oil have been cracked using the newly fabricated 20 gallon reactor. A fairly constant yield of 2-octanol and slightly varying yields of sebacic acid have been obtained.

## OC-VIII. COMPOUNDS FOR WATER EVAPORATION CONTROL

The following types of compounds were prepared and supplied to the Physical Chemistry Division: (1) Higher alcohols containing one to three units of ethylene oxide, prepared by condensing the corresponding alkyl halide with the monosodium salt of the glycol or by catalytic condensation of ethylene oxide with the alcohol. (2) Glycol esters (mono- or di-) of palmitic and stearic acids. (3) Mixed ethyl esters of hydrogenated kokum butter and mustard oil.

## OC-IX. MICROANALYSIS

(1) Routine work

1834 analyses were carried out for various elements and functional groups in organic compounds. Of these 1749 were done for the NCL and 85 for outside institutions.

(2) Research work

(a) A method for the direct micro determination of oxygen in organic compounds is being studied, using a low temperature (700°) for the pyrolysis of the compound instead of 1150° used in the method of Unterzaucher.

(b) A method for the determination of active hydrogen is being investigated using sodium borohydride-diborane complex.

(c) A method for the micro determination of carbonyl groups by oximation was standardized, but it could not be used for sterically hindered carbonyls.

## OC-X. NATURAL AND SYNTHETIC COLOURING MATTERS

(1) Lac dye

Two colouring matters, "laccaic acid" and erythrolaccin, were isolated and studied earlier by Dimroth and others. Erythrolaccin, for which Tschirch and Lüdy proposed the tentative structure 1,2,4,7-tetrahydroxy-5-methylanthraquinone, is 1,2,5,7-tetrahydroxy-3-methylanthraquinone (Tet. Letters, 1959, No.6, 22). On the basis of Dimroth's extensive experimental work Mayer and Cook assigned the structure 2-acetyl-3-ethyl-1,4,6-trihydroxyanthraquinone-7,8-dicarboxylic acid to laccaic acid. "Laccaic acid"contains 1-2 per cent N present as $NH_2$ (van Slyke), and is a mixture of several closely related colouring matters, from which a N-free and chromatographically homogeneous dye, red needles from hot water, can be isolated. The structures of this and related colouring matters are under investigation.

(2) Constitution of morellin

In connection with the identification of one of the degradation products of morellin a new method has been developed for the synthesis of 2,2-dimethylchromanones and 2,2-dimethylchromanes.

(3) The colouring matters of *Artocarpus integrifolia*

Two new flavonoid pigments, artocarpetin and artocarpanone, have been isolated from the heartwood of *Artocarpus integrifolia*. Their structures have been proved by colour reactions, absorption spectra, degradation and synthesis. Artocarpetin is 5,2',4'-trihydroxy-7-methoxyflavone and artocarpanone is the corresponding flavanone. The resorcinol pattern of the B-ring is of interest, since only two natural flavones of this type (morin and artocarpin) are known, both of which occur in *Artocarpus integrifolia*; artocarpanone is the first natural flavanone with hydroxyl groups in the 2',4'-positions. This wood also contains cyanomaclurin, which Appel and Robinson have shown to be probably constituted as the cyclic hemiketal of 5,7,2',4'-tetrahydroxy-3-ketoflavan and which is therefore closely related in the hydroxylation pattern of both the A and B-rings to morin, artocarpin, artocarpetin, and artocarpanone.

The action of boiling hydrobromic acid in acetic acid or hydriodic acid and acetic anhydride under prescribed conditions on 5,7,2',4'-tetramethoxyflavone leads to 5,4'-dihydroxy-7,2'-dimethoxyflavone.

Artocarpin contains two $C_5H_9$ side chains in the 3- and 6-positions. By the ozonization of the di- and tri-methyl ethers of artocarpin and the dimethyl ether of dihydroartocarpin it has been found that the 3-position is occupied by $-CH_2-CH=CMe_2$ and the 6-position by $Me_2CH-CH=CH-$. Synthetical experiments are in progress to confirm the structure.

## (4) Natural anthraquinone colouring matters

Further work has been carried out on new methods for the synthesis of naturally occurring hydroxyanthraquinones (cf. Festschrift Arthur Stoll, 1957, p. 360). Using the new procedures, chrysophanol, rhein, emodin, physcion and islandicin have been synthesized. A synthesis of the 2- and 7-hydroxymethyl derivatives of 1,3,8-trihydroxyanthraquinone has shown that versicolorin, a metabolite of *Aspergillus versicolor* isolated by Japanese workers, does not possess either of these structures. Aloe-emodin and citreorosein have been synthesized by the diborane reduction of the acetyl derivatives of the corresponding carboxylic acids. A new general method has been developed for the reduction of anthraquinones to the corresponding anthracene derivatives by treatment with sodium borohydride and boron trifluoride etherate. During exploratory experiments on the synthesis of endocrocin, which has been isolated from a lichen and a fungus by Japanese and other workers, 1-hydroxy-3-methyl-anthraquinone-2-carboxylic acid has been synthesized. The synthesis of 1,6,8-trihydroxy-3-methylanthraquinone-2-carboxylic acid (emodin-2-carboxylic acid), the structure accepted at present for endocrocin, presented difficulties in the final stages, but an examination of the product, although it has not yet been obtained in analytical purity, casts doubt on the structure of endocrocin. It is also clear from the infra-red spectrum of endocrocin that an alternative structure (emodin-ω-carboxylic acid) will have to be considered and a compound with this authentic structure is being synthesized. Some of the known and new anthraquinone derivatives are being submitted to antitubercular and antitumour tests outside the NCL.

## (5) Citrinin

The total synthesis of citrinin has not yet been achieved. This is now being attempted by a series of reactions which are approaching completion.

## (6) Isoflavones

2,4,6-Trihydroxy-3-methoxyphenyl 3,4-dimethoxy-5-nitrobenzyl ketone has been synthesized, and its cyclization to the corresponding isoflavone is being studied with the object of synthesizing irigenin following the general method by which tectorigenin was synthesized. Incidentally, a new procedure for the cyclization of *o*-hydroxyphenyl benzyl ketones to isoflavones has been developed.

(7) Azoic dyes

The action of cyanuric chloride and 2,4-dinitrochlorobenzene on *o*-hydroxybenzanilides has been studied, and it has been shown that the mechanism of the reaction, which results in the formation of *N*-cyanuryl and *N*-dinitrophenyl derivatives, consists partly or wholly of a nucleophilic attack by the nitrogen atom of the anilides; a Smiles rearrangement of the dinitrophenyl ether may be simultaneously involved. The reactions are useful for the hydrolysis of such anilides and the determination of the constitution of new azoic coupling components of the Naphtol AS type. Thus it has been found that Naphtol AS-RS is the 4-chloro-2-methoxy-5-methylanilide of 2-hydroxy-3-naphthoic acid; and Naphtol AS-KN is the α-naphthylamide of 3-hydroxydibenzofuran-2-carboxylic acid.

(8) Anthraquinonoid vat dyes

Work on the analysis of anthraquinonoid vat dyes by chromatography on alumina at 100-150$^\circ$ and the determination of the structures of several dyes has been continued.

## OC-XI. THE CONSTITUENTS OF CAPPARIS MOONII

Work on the chemistry of the constituents of the fruits of *Capparis moonii* was initiated at the request of a Bombay physician, according to whom the powder of the fruits is effective in the treatment of tuberculosis. Although *in vitro* and mouse tuberculosis tests carried out at the CDRI, Lucknow, and in a Russian institute have given negative results, the chemical investigation has been continued. It has been found that the fruits contain an alkaloid, now identified as *l*-stachydrine. β-Sitosterol is also present. Two other crystalline constituents have been isolated and work on their structures is in progress.

## OC-XII. ORAL ANTIDIABETIC AGENTS

In collaboration with a member of the staff of the Armed Forces Medical College several Indian plants alleged to have antidiabetic properties have been screened, generally with negative results. Simultaneously a synthetic programme in this field has been undertaken.

# ESSENTIAL OILS

## EO-I. SYNTHETIC PERFUMERY MATERIALS

For some time we have been trying to develop practical methods for the synthesis of macrocyclic musk-line compounds, such as civetone, dihydrocivetone, exaltone,and exaltolide, using easily available indigenous raw materials. In this connection we have reported earlier the results of our investigations, specially on the synthesis of civetone and dihydrocivetone, including their successful preparation on a pilot plant scale. Further investigations were carried out as follows :

### (1) Civetone, isoambrettolide and dihydroambrettolide
(July 1959)

During this year, aleuritic acid has been successfully converted to civetone, isocivetone, dihydroambrettolide and isoambrettolide. $C_{15}$ and $C_{16}$ $\omega,\omega'$-dicarboxylic acids with and without double bonds, which have also been previously prepared from aleuritic acid, are being cyclized to cyclohexadecanone, exaltone and exaltolide.

### (2) Exaltone and exaltolide (Pilot Plant Project)
(April 1959)

These two are probably the most widely used macrocyclic musk-like compounds. A method was previously developed by us for the synthesis of exaltone from mustard oil. This method was taken up for pilot plant investigation during the year and is expected to be completed in 1960-61. A new and direct method which has been recently developed for the synthesis of exaltolide is also now undergoing pilot plant trials. Our objective is to prepare 5 lb. each of exaltone and exaltolide. Exaltone and exaltolide are suitable substitutes for natural musk.

The Indian Board of Wild Life, which is interested in stopping extermination of musk-deer for the collection of musk-pods, has taken note of our investigation. The Board in collaboration with the CSIR recently circulated a Press Note to enlighten interested parties in this connection. This report has received wide publicity and enquiries have been received by us and also the Secretary, NRDC,for further details.

### (3) Muscone
(July 1959)

Muscone is the perfumery principle obtained from musk-deer. After achieving the synthesis of exaltone and exaltolide, it was felt desirable to establish a synthesis of muscone. We have been attempting to develop the use of oleic acid as a raw material for this purpose. Though some progress has been made towards the synthesis of the requisite $C_{16}$ dicarboxylic acid, yields at some of the stages are not satisfactory.

### (4) Dihydrojasmone and isojasmone (Pilot Plant Project)
(June 1959)

These two products are suitable substitutes for jasmone, which is one of the main odorous principles of jasmine concrete. The method of synthesis which has been standardized in this Laboratory previously was taken for pilot plant trials with a view to preparing 25 lb. each of dihydrojasmone and isojasmone. About 13 lb. of dihydrojasmone have been so far prepared; the remaining portion will be prepared during 1960-61.

### (5) Menthol
(August 1958)

Experiments on the synthesis of menthol from citronella oil have been continued . About 25 lb. of citronellal were purified and then converted through isopulegol acetate, iso-pulegol, and by hydrogenation to a mixture of menthol and its isomers. Experiments are in progress to isolate pure menthol through its boric and chloroacetic ester. In this connection 20 lb. of $\alpha$-terpineol have also been hydrogenated under pressure to the corresponding dihydro derivative.

### (6) Coconut aldehyde
(July 1959)

$\gamma$-Nonalactone (coconut aldehyde) is used as a food flavouring agent. Optimum conditions for its preparation by cyclising the condensation product of heptaldehyde and malonic acid are being studied.

### (7) Utilisation of sandalwood oil hydrocarbons
(July 1959)

It appears that 25,000 lb. of sandalwood oil hydrocarbons are available every year in the Government Sandalwood oil Factory, Mysore. Compared to the santalol-rich sandalwood oil of commerce, it finds only limited use. With the object of widening its utility, pure $\alpha$- and $\beta$-santalenes have been separated by distillation and then converted to oxygenated bodies by various reactions. In this connection various aspects of the chemistry of tricycloeka-santalic acid obtained by oxidation of $\alpha$-santalene and $\alpha$-santalol are being investigated.

### (8) Ionone
(July 1959)

Some aspects of the method of preparation of $\beta$-ionone previously established in this Laboratory required re-checking. For this purpose about 20 lb. of pseudoionone have been prepared and part of it cyclised under different conditions with a view to obtaining the best yield of $\beta$-ionone. A comparable method patented in Czechoslovakia was also examined simultaneously.

(9) Irone
(August 1959)

With a view to developing a synthesis of irone from turpentine, substantial quantities of pinonic acid have been obtained by oxidation of pinene. It was found that for preliminary investigation the use of permanganate as an oxidizing agent was convenient.

(10) Hydroxycitronellal and allied products
(July 1959)

Several experiments were carried out to prepare hydroxycitronellal or allied products through epoxidation of citronellal and subsequent reduction of the epoxide.

(11) Pure fatty alcohols
(March 1959)

Pure stearyl and palmityl alcohol (A.R.Grade), required by the Physical Chemistry Division for water-evaporation experiments, were prepared by initially isolating the ethyl or methyl esters of stearic and palmitic acid by careful batch-strip fractionation and then by subsequent reduction with lithium aluminium hydride.

(12) Research chemicals

About 25 special research chemicals have been prepared during this year. A few of these have been supplied to sister research organizations.

## EO-II. ESSENTIAL OILS

(1) Agarwood oil
(January 1958)

Isolation and characterisation of agarol, one of the main odorous constituents of agarwood oil, was reported last year. The structure and stereochemistry of another important constituent of the oil has since been elucidated. It is a monoethenoid keto-alcohol similar to hydroxydihydroeremophilone. But unlike the latter, it is a true isoprenoid, and has been successfully converted to selinane, thus confirming the stereochemistry at the ring juncture.

(2) Costus root oil
(January 1958)

Costus root oil is one of the important essential oils of Indian origin. Development of a new method for the isolation of this oil and separation of its various constituents have been reported previously. By systematic examination, the structure, stereochemistry and absolute configuration of costunolide have been completely established. Hexahydrocostunolide has a pleasant exaltone-like odour. Costus root oil has also been found to contain a large number of other oxygenated compounds not reported previously.

The structure of saussurea-lactone previously investigated at the Forest Research Institute was re-examined with a view to examining its relationship with santanolides or alantolactones. However, no correlation has been found so far.

Dehydrocostuslactone, which is one of the major constituents of costus root oil obtainable by our method, was examined with a view to confirming some aspects of its stereochemistry and also to convert it to commercially useful azulenes.

About 40 kg. of costus root oil extracted earlier were delactonised and a large number of samples of this was sent to various parties for olfactory evaluation. Delactonised oil appears to be acceptable to the industry, and 20 kg. have been supplied to a French firm.

## (3) Vetiver oil
(January 1958)

Several new sesquiterpenoid hydrocarbons have been isolated from South India and Musangar varieties, one of which was common to both. The constitution of another hydrocarbon occurring in the South Indian oil has been elucidated.

A crystalline eudalenic alcohol isolated from Musanagar vetiver oil has been investigated and its structure fully established. It is the laevo antipode of junenol previously examined by Sorm and collaborators. In this connection the synthesis of two isomers of dihydrojunenol has been carried out using santonin as the starting material. This investigation completes the absolute configuration of junenol and should prove to be useful for the preparation of optically pure selinanes. Leavo-junenol is the only eudalenic compound known to have wrong absolute configuration at all the centres of assymmetry. It may be one of the factors responsible for the rather inexplicable leavo-rotation of North Indian vetiver oil.

Progress has also been made on the chemistry of the ketonic and alcoholic constituents of Indian vetiver oil. They are different from the corresponding components of Java vetiver oil.

## (4) Camphor-rich Ocimum oil
(July 1959)

About 60 kg. of the leaves of Ocimum kilimanjaricum were distilled to isolate the camphor-rich oil (1.3 kg.). The work was done in collaboration with the Chemical Engineering Division.

## EO-III. RESIN & RESIN OILS
(March 1958)

Resin oil from Shorea robusta, commonly known as chua oil, was examined. On careful scrutiny it was found to be composed of a very large number of almost inseparable components. In the lower boiling fraction, the presence of p-cymene and ocimene has been confirmed. The higher boiling portion contains several sesquiterpene hydrocarbons. The structure of two of these has been elucidated. Chua oil also contains several unidentified azulenes, free cadalene and a few other alkylnaphthalenes and a $C_{14}$ ketone. The letter seems to be the only oxygenated compound present in the neutral fraction of chua oil. Some of the components of the parent resin have also been isolated by partition and column chromatography.

## PROJECTS TERMINATED OR CONCLUDED

Work on the following projects has been completed:

(1) Civetone - Pilot plant work.

(2) Dihydrocivetone - Pilot plant work.

(3) Wild ginger oil - General chemical investigation.

# BIOCHEMISTRY

## B-I. STEROID SYNTHESIS
(January 1959)

Kurchi alkaloids are nitrogen-containing steroids which appear to be attractive starting materials for the synthesis of the mineralo-corticoid hormone, aldosterone. The object of this work is to develop a method of synthesis of aldosterone from the Kurchi alkaloids. Holarrhimine was converted in good yield to 18-hydroxyprogesterone by N-chlorination, dehydrochlorination and hydrolysis. Conessimine was converted to 3 $\beta$-N-dimethylconkurchine by N-chlorination and dehydrochlorination. It was also converted by cyanogen bromide treatment to conimine from which 18-hydroxyprogesterone was prepared by the method of Jaeger *et al*. The microbiological conversion of 18-hydroxyprogesterone or its derivatives to the 11-$\beta$-compounds is under investigation. The action of nitrous acid on holarrhimine was found to yield a number of products, six of which were isolated in crystalline form. One (m.p.166-167°) was nitrogen-free ($C_{21}H_{31}O_2$), and was characterized as 3$\beta$-hydroxy-5-pregnene-18, 20-oxide; and a basic compound ($C_{21}H_{35}O_2N$, m.p.225°) was tentatively identified as 3$\beta$-18-dihydroxy-20-$\alpha$-amino-$\Delta^5$-allopregnene.

## B-II. BIOSYNTHESIS & METABOLISM

The object of this work is to study the metabolism and synthesis of pectic substances and proteins. Preliminary work on this project was begun in January 1959.

### (1) Pectin metabolism

Galactose-1-phosphate, galacturonic-1-phosphate and galacturonic acid methyl ester were synthesized. Chromatographic methods were developed for the separation of galacturonic acid, glucuronic acid and their-1-phosphates. The formation of $P^{32}$-labelled uronic acid derivatives in the presence of extracts of mung bean seedlings is under investigation.

### (2) Proteins

(a) A cell-free system which gave a net increase of 20 to 30 per cent protein in the presence of ATP, amino acids and other co-factors was obtained from mung bean seedlings. Attempts to show net synthesis of specific enzymes such as glucose-6-phosphate dehydrogenase, glyceraldehyde phosphate dehydrogenase and aldolase were, however, unsuccessful. Active tyrosine and phenylalanine activating enzymes were found to be present in some plant seedling extracts and are being purified.

(b) The amino acid composition of the fibroins from four indigenous silks (Mulberry, Tussa, Muga and Eri) was determined in the previous year. This study was extended to the sericins from these silks. The sericins were found to differ from the fibroins in having a higher serine, lysine and aspartic acid content and a lower glycine and alanine content. Ultracentrifugal studies on mulberry silk fibroin in lithium thiocyanate solution (0.25, 0.50 or 1.0 saturation) showed the presence of a single component with a molecular weight of 40,000. When the lithium thiocyanate concentration was reduced to one-eighth saturation or less, two components were observed which had a weight-average molecular weight of 2.5 to 3.0 x $10^5$ - indicating disaggregation of the protein to small units in high concentrations of LiCNS and aggregation to larger molecules on reducing the salt concentration.

## B-III. MICROBIOLOGY

The objectives of this work are : (1) maintenance of the National Collection of Industrial Microorganisms, (2) screening for improved strains of industrially important organisms, and (3) fundamental studies on microbial metabolism and new fermentations.

### (1) National collection of industrial micro-organisms

The main objects of the culture collection are to collect, maintain and distribute micro-organisms of importance for research and industry. The collection contains about 1100 bacteria, yeasts, fungi and other non-pathogenic micro-organisms which are made available to scientific and industrial institutions. The routine subculture and maintenance of the cultures were continued; fifty-two cultures were added to the collection during the year and 320 cultures were despatched to 112 institutions. The "Directory of Collections of Micro-organisms and List of Species Maintained in India" was first published in 1953 in collaboration with other Commonwealth countries. Work on the compilation of a revised Directory was completed during the year. It will be published by the British Commonwealth Scientific Organization along with the Directories of other Commonwealth countries.

### (2) Microbiological production of sulphur
(1950)

The objective of this work is the production of sulphur by the microbiological reduction of calcium sulphate using undigested sewage sludge as the source of organic material. Consistent yields of sulphides (1.4 to 1.8 g. per 100 volumes of sludge) were obtained with sewage sludge as the reducing agent and gypsum as the sulphate source. The yields were not significantly altered when $H_2S$ was swept out for only 16 hours during the day. Low-grade Rajasthan gypsum and calcium sulphate obtained as a by-product in the manufacture of common salt were found to be suitable for reduction.

Work on the sulfurylase of the sulphate reducing bacteria, D.desulphuricans, was completed. A new enzyme which catalyses the liberation of inorganic phosphate from ATP in the presence of sulphite was found in the insoluble fraction of the bacterial cells. The products of the reaction were shown to be ADP and inorganic phosphate, and not AMP and pyrophosphate as in the case of sulphurylase. There was no exchange of radioactive phosphate with ATP in the presence of the enzyme and sulphite. Two different pyrophosphatases were shown to be present in the bacteria, a soluble enzyme with a pH optimum at 8.0 and requiring $Mg^{++}$ and an insoluble enzyme with a pH optimum at 6.0 and requiring $Co^{++}$ and $K^+$ for maximum activity.

## (3) Screening studies

(a) Vitamin $B_{12}$ - Six bacterial isolates were tested for vitamin $B_{12}$ production, but the maximum yield with or without precursor was only 0.25 mgm/litre compared to 2.0 mgm/litre obtained with other isolates.

(b) Citric acid - The object of this work was to increase the depth of the medium and the yield of citric acid in the process which was developed in this Laboratory. The effect of the concentration of sugar and other constituents, the relative humidity, aeration rate and temperature were studied, and the optimum conditions were determined for obtaining yields of 60 per centor more with a medium depth of 5.0 cm. compared to a depth of 2.5 cm. used previously. Similar yields were obtained with large trays containing 30 litres of medium. It was found that some varieties of cotton leaves contained large amounts of citric acid. The feasibility of utilizing this agricultural waste for the production of citric acid is being investigated.

## (4) New fermentations and fundamental studies

(a) Microbiological conversion of terpenes (January 1959) The object of this work is to study the conversion of terpenoid hydrocarbons to essential oils by micro-organisms. A new microbiological oxidation by which terpenoid hydrocarbons are converted to oxygenated compounds was developed. A strain of Aspergillus niger was found to oxidize $\alpha$-pinene rapidly and among the products of oxidation, d-cis-verbenol, d(+) verbenone and d(+) trans-sobrerol were identified. $\alpha$-Santalene was converted by the same strain to teresantalic acid and teresantalol. The transformation products from other terpenes such as $\Delta^3$-carene are under investigation.

(b) Submerged culture of plant tissues (August 1959) - The object of this work is the cultivation of cells from different plant tissues under conditions similar to those used with micro-organisms in order to study the properties of these cells, which may be regarded as a new class of micro-organisms, and to obtain useful products characteristic of plant materials. Six different plant tissues were successfully cultivated on solid or in liquid media and callus tissue from an indigenous variety of beans, which was characterized by very rapid growth, was selected for further study. The nutrient requirements for these cells were determined and the best growth was found to be obtained on White's medium containing coconut milk, yeast extract, and 2-4-dichlorophenoxyacetic acid. Encouraging results were obtained on transfer of the cells to shake flasks and fermentors with vigorous aeration. Yields of 40 g. of wet tissue per liter were obtained in preliminary experiments under submerged conditions.

(c) Fumaric acid fermentation - Studies on the mechanism of fumaric acid formation and the metabolism of R.nigricans were undertaken. Arsenite and malonate were found to have no effect on fumaric acid formation whereas iodoacetate, fluoroacetate, arsenate and fluoride were inhibitory indicating that the EMP pathway and the aconitase reaction were probably involved in the conversion of glucose to fumarate. Studies on the enzymes in cell-free extracts showed the presence of several of the glycolytic and citric acid cycle enzymes, but fumarase activity was negligible.

## B-IV. BACTERIAL DIASTASE

The object of this work is to develop a process for the production of bacterial diastase primarily for use as a desizing agent in the textile industry.

Pilot plant work on this project was begun in December 1957.

A non-technical note on the production of bacterial diastase by submerged fermentation using specially selected strains of bacteria was prepared and referred to the National Research Development Corporation, who have arranged for the commercial exploitation of the process. Further modifications and improvements of the process were carried out during the year.

A method for the production of protease by submerged fermentation was developed.

## PROJECTS TERMINATED OR CONCLUDED

### 1) Microbiological production of sulphur.

Since pilot plant work on the chemical reduction of gypsum with lignite is being carried out at Regional Research Laboratory, Hyderabad; this project was terminated.

### 2) Vitamin $B_{12}$

Since the production of vitamin $B_{12}$ is to be undertaken in the country by a commercial firm, this project was terminated.

# POLYMER CHEMISTRY

## P-I. FUNDAMENTAL STUDIES IN HIGH POLYMERS

### (1) Low polymers of ethylene

(June 1958)

Low polymers of ethylene (mainly hexamers), obtained by polymerisation of ethylene using aluminium chloride in ethylene dichloride, were used for alkylation of benzene. A variety of conditions involving change of solvent media, temperature of reaction, purity of catalyst, etc., both in ethylene polymerisation and alkylation reaction, was tried in order to produce the desired alkylbenzene, but without success. Likely impurities arising out of autoxidation of the polymer that may inhibit the alkylation reaction were removed by various methods prior to alkylation, but results did not impyove. On the other hand, parallel alkylation using a straight chain olefin, e.g. decene-1, proceded smoothly, and essentially mono-substituted alkylbenzenes were obtained in good yield. The constituents of the ethylene polymer are being investigated.

Among catalyst combinations other than aluminium chloride tried for the polymerisation of ethylene, metal alkyls in conjunction with a suitable titanium compound appear promising for the controlled polymerisation reaction. Conditions are being standardised.

### (2) Polymerisation reactions

(1958)

(a) After the kinetic evidence obtained for the induced decomposition of N-nitrosoacetanilide by polymethyl methacrylate radicals, N-nitrosocarbanilide was used as initiator, when the formation of lower molecular weight polymers indicated induced decomposition of the initiator. But the kinetic method could not be used for evaluation of $K_d$ since the conversion time graphs did not show sufficient curvature. Studies were continued with NN'-dimethyl NN'-dinitroso terephthalamide in the presence of other initiators such as benzoyl peroxide to determine the nature of the molecular chain interruption. Since the compound does not initiate polymerisation, its effect on rate of polymerisation and molecular weight of polymers was followed. It has been observed that retardation of rate and reduction in chain length were proportional to the concentration of the amine employed.

(b) The polymerisation of methyl methacrylate in aqueous medium initiated by hydrazine in presence of oxygen was investigated in detail. The study of the variation in the rate of the reaction at constant hydrazine and metal ion concentration but with varying monomer concentration indicated a first order rate law with respect to monomer concentration. The rate was also found to be directly proportional to metal ion concentration and the pH of the medium. The results were consistant with a mechanism of inihition involving the hydrazyl radical formed by a direct reaction between hydrazine and metal ion. The formation of radical intermediates in the conversion of cuprous to cupric state and also a chain termination step involving polymer radical, cuprous ion and oxygen are also indicated. That the nitrogen containing radicals produced from hydrazine are involved in initiation has been separately confirmed by the detection of nitrogen in the polymer by degradation.

(c) The graft-polymerisation of methyl methacrylate with natural rubber initiated by the redox system based on hydrazine was investigated in detail. The optimum conditions for maximum graft copolymer formation were standardised and 10 lb. batches of the material were prepared. The test conditions for the vulcanization of the product were arrived at and the mechanical properties of the vulcanizates have been determined. Thus the tensile strength, shore hardness and abrasion resistance of the graft copolymer vulcanizates were found to be substantially higher than those of natural rubber vulcanizates.

### (3) Solution properties
(1956)

Further experimental evidence has been collected to show that the maxima-minima effects observed in the viscosity behaviour of polymer solutions at high dilutions result from the configurational changes of macromolecules in solution. It has been also shown that adsorption effects which were earlier considered as insignificant in the case of hydrocarbon polymers such as polystyrene and natural rubber may be of importance in polymers with polar groups, e.g. polymethyl acrylate.

As a result of the studies on the viscosity behaviour of unfractionated polymethyl acrylate in solvent—nonsolvent mixtures at 30°, it has observed that the Huggins' slope constant k' at the precipitation point is independent of the nature of the solvent—nonsolvent. The studies were extended to the possible effect of temperature, and the viscosity behaviour was examined in two solvent-nonsolvent systems at 40°. It was observed that k' at the precipitation point is independent of temperature as well.

A max. value of 0.5 for the Huggins' slope constant k' obtained from viscosity measurements has led to a one-parameter method for molecular weight determination in polymers. The method accommodates the data available in literature.

## P-II. ION EXCHANGE

### (1) Cation exchange resin from CNSL (Pilot Plant Project)

The pilot plant project was successfully completed by the end of December, 1959. The quantity of resin produced and other details are given below :-

| | | | |
|---|---|---|---|
| i) | Total quantity of good quality CNSL resin produced up to 31st December, 1959. | ..... | 9538 lb. |
| ii) | Good quality resin sold to outside parties. | ..... | 3828 lb. |
| iii) | Resin sent as samples to outside parties. | ..... | 82 lb. |
| iv) | Resin of good capacity in stock. | ..... | 5628 lb. |
| v) | Resin of lower capacity obtained during standardization experiments. | ..... | 1200 lb. |

A detailed report on the project has been prepared. The commercial exploitation of the process has been recently released to M/s. Tulsi Industries, Poona, by the NRDC.

## (2) Water softening and demineralisation

(a) The water softening performance of the CNSL resin in the Pimpri plant for a period of about 18 months has been studied and good operational performance has been observed. The effect of salt dosage for regeneration was studied.

(b) The CNSL cation-exchange resin in the hydrogen cycle is being used in conjunction with an anion-exchange resin prepared in the laboratory and demineralisation performance is being studied.

## (3) Cation exchange resins - polystyrene base

(April 1958)

A systematic study of the sulphonation of cross-linked polystyrene to get cation-exchange resin was made to standardize the conditions for production of the resin; 70 lb. of the resin (cap. 4.5-5.0 meq/gram) were then prepared for use in rare-earth separations.

## (4) Anion-exchange resins

(April 1958)

(a) Melamine base - After conducting extensive studies towards standardisation of the procedure for preparation of this resin, large scale preparation was undertaken using commercial grade chemicals. A large stock of the resin has been prepared for conducting exhaustive performance studies which are under way.

(b) Polyvinyl chloride base - Conditions were standardised for the preparation of the resin with the highest capacity. Using commercial grade chemicals the work has been taken up on a larger scale in a kettle. The silica removal capacity of this resin is also under study.

## (5) Electrodialysis

Some samples of rubber-based membranes were prepared according to Ind. Pat. No. 55546. Concentration potentials with different types of cation-exchange membranes were measured in a cell using different concentrations of potassium chloride solutions.

## P-III. RUBBER

A major development during the year was the establishment of a Rubber Research Project under the joint auspices of the CSIR and the Indian Rubber Manufacturers' Research Association on 1st September, 1959. Under this project, two of the earlier problems (2a and 2b) were continued, and two new problems (3a and 3b) were taken up; the remaining problems (1a to 1d) were discontinued.

### (1) Problems discontinued (August 1959)

(a) Thermally conductive rubber (January 1958 to August 1959) - After completing studies on thermal conductivity and chemical resistance of Neoprene and GRS mixes, the work was wound up. Data collected are of use in selecting the appropriate composition resistant to a particular chemical up to 60° and having improved thermal conductivity compared to usual rubber compositions.

(b) High-impact ebonite (February 1958 to August 1959) Experiments were continued on utilisation of battery scrap received from a firm for making ebonite. Tests on impact strength, chemical resistance and softening point of the ebonite were carried out. The chemical resistance was within the specified limit (B.S. 454-1938).

(c) Flame-proof and fire-proof rubber (February 1958 to August 1959) - Preparation of chlorinated compounds was continued; chlorinated liquid rubber and polyesters were made and tested according to BS434 (1953) on cable braid. Chlorinated polyesters passed the flame resistance test.

(d) Speeding up of cures (December 1958 to August 1959) - Work was continued on evaluation of the aldehyde amine accelerator prepared in the Laboratory and the compound was found to be comparable to Vulcafor BA in hard rubber compositions, though slower in soft rubbers. This result was confirmed by small scale trials in the industry. Ageing characteristics of the accelerator were satisfactory.

### (2) Old problems (continued)

(a) Rubber-base adhesives (September 1957) - Tests on the performance of adhesives covered by Ind. Pat. No. 65977 carried out by a few firms showed that they could be satisfactorily used for bonding aluminium to aluminium or aluminium to rubber; for bonding aluminium to felt a modification of its solution viscosity was necessary and was carried out.

From other formulations previously investigated, phenolic resin rubber blends were selected for further work, as they represent an important class of modern commercial adhesives. Various resins and nitrile rubber mixes were prepared and tested both by heat-curing and room temperature bonding. Shear strength in lap-joint in steel recorded up to 2250 p.s.i., the average figure being 1800 p.s.i. Room temperature bonding with a formulation developed here compared favourably with 'Pliobond' when tested for aluminium, steel, fabric, leather and rubber (similar and dissimilar surfaces). All stages of the preparation and testing of the adhesives are being standardized.

(b) Microcellular rubber (July 1958) - The blowing agent developed earlier was tested on a small scale by two firms and found to be very promising. Trials by three other firms are continuing. Laboratory evaluation of its performance in natural and butyl rubbers showed that it compares favourably with Vulcacel BN, a standard commercial blowing agent.

(3) New problems
(September 1959)

(a) Identification of antioxidants, antiozonants and copper inhibitors - The object is to develop simple methods of identifying common commercial antioxidants in original form or in rubber compounds, uncured and cured, unaged and aged (heated at 70° for 1 to 7 days). Tests investigated were based on known colour reactions and paper chromatographic techniques, and were tried on ten antioxidants collected from the industry. Several spot tests and colour reactions on paper and in test tubes were developed; these have not been reported in literature for identifying these ten antioxidants.

(b) Processing of indigenous China clays - A detailed study on Indian clays from eight sources including Palyangadi and Thirthahalli was undertaken. The principal factors investigated were removal of non-kaolinite impurities, removal of copper, particle size distribution, and pH. Washing and screening (through 250 mesh) of Kannapuram clay produced a marked improvement in tensile strength of a natural rubber compound; it became comparable with standard American clay Suprex. Clays from Palyangadi and Thirthahalli also showed promise of being improved in a similar way. Fractionation of clays by sedimentation under different conditions was undertaken to obtain samples for study by differential thermal analysis (DTA). The process of air flotation for fractionation of clay according to particle size is under study. Open steam treatment of clays was carried out in a vulcanizer and the results are to be examined by DTA. It is evident that some of the clays can be made reinforcing fillers by suitable treatment.

## P-IV. POLYSTYRENE
(1956)

This work aims at developing a standard procedure for the suspension polymerisation of various monomers, particularly styrene, and to extend it to the preparation of expandable beads. Work on this project was carried out during 1953-54 and then terminated. It was resumed in 1956. Using 40-50° petroleum ether (10-20 per cent) as blowing agent about 8 lb. of styrene were polymerised in sealed cans at different temperatures and in different proportions of the blowing agent. It was found that not more than 10 per cent of the blowing agent was necessary to have a product of reasonable foam density (between 1-2 lb./cu.ft.). A 2-gallon pressure kettle which was procured recently for suspension polymerisation experiments is under test.

## P-V. POLYURETHANES
(1957)

The objective of this project is to study the chemistry and develop techniques for the preparation of polyurethanes in various forms, such as flexible and rigid foams and insulating coating compositions. During the last few years polyurethanes have been used increasingly abroad in view of their outstanding physical and chemical properties. The period under review was mainly spent in making further improvements in the machine for the continuous production of foams. In view of the non-availability of suitable metering equipment a device whereby the regulated movement of a piston of the syringe containing the reactants delivers measured quantities at a specified rate was developed. A 1,000 cc. metal syringe for the prepolymer and a 50 cc. glass syringe for water-catalyst were used. Several modifications and trials in the mixing-head were made so as to produce a continuous flow of the well mixed reactants, which gave foams of uniform texture. It is now possible to produce 12" x 12" or even larger sizes of foam with a uniform cell structure.

The properties of the flexible foams so produced are :

| | | |
|---|---|---|
| Density | - | 3.3 lb./cu.ft. |
| Tensile strength | - | 53-66 p.s.i. |
| Compression set per cent | - | 20 |
| Tear strength | - | 3.5-3.7 lb./inch. |

The preparation of rigid foams by making a few modifications in the above device is under study. A standard technique for the large scale (5 lb. batch) preparation of polyesters was evolved, and polyesters with the required properties were prepared from different dicarboxylic acids and glycols.

## P-VI. OTHER PROJECTS

### (1) Can scaling composition

The commercial exploitation of the process developed for the preparation of can-sealing composition has been entrusted by the NRDC to a firm. The representative of the firm familiarized himself with the various steps involved in its production. Work on the project has been terminated.

### (2) Foundry core oil
(1957)

The details of the process for the preparation of foundry core oil have been released free of cost to interested parties. Many enquiries were attended to, and samples were prepared for tests by foundries.

Work on the preparation of an oil-free core binder has been undertaken for a firm and encouraging results have been obtained.

## (3) Surface coatings

(a) Modified U.F. resin for bobbins - Samples of modified urea resins and bobbins coated with formulations based on these resins were supplied to various parties. The process is being released by the NRDC.

(b) Styrenated alkyds (1959) - Copolymerisation of styrene with fatty acids and subsequent conversion into alkyds were carried out. Enamel formulations based on these alkyds showed much better film-forming properties than ordinary alkyds.

## (4) Pressure sensitive adhesive tapes

Preparation of adhesive compositions and their coating on a cellophane base was demonstrated to the representatives of a firm in Bombay to whom the process has been released by the NRDC. Special adhesive formulations for use in pressure-sensitive adhesive paper base photo corners were developed.

## (5) Porous rigid filters

The construction of a tube well using 100' of rigid sand filters developed and prepared at the Laboratory was completed in April, 1959, and it has so far given satisfactory performance.

## (6) Miscellaneous

(a) Lac dye - The dye was evaluated in typical natural rubber compounds for its antioxidant effects and was found to have some protective action.

(b) Indigenous barytes - The evaluation of three samples of Andhra barytes, processed in the Inorganic Chemistry Division, in rubber compounding was carried out in comparison with two known samples obtained from a rubber manufacturer.

## PROJECTS TERMINATED OR CONCLUDED

## P.II. - ION-EXCHANGE

1) Cation-exchange resin from commercial cashew nut shell liquid (Pilot Plant Project). Work has been successfully completed and process released to industry.

P.III - RUBBER

1a) Thermally conductive rubber.
1b) High impact ebonite.
1c) Flame-proof and fire-proof rubber.
1d) Speeding up cures.

Work on the above problems was discontinued as per recommendation of the Indian Rubber Manufacturers' Research Association (I.R.M.R.A.)

P.VI - OTHER PROJECTS

1) Can-sealing composition.
2) Foundry core oil.
3) Pressure sensitive adhesive tapes.

Work on the above problems has been successfully completed and processes released to industry.

3a) Modified Urea-Formaldehyde resin for bobbins.
5 ) Porous rigid filters.

Work has been completed and the release of the processes is under consideration of the NRDC.

6a) Lac dye :- Exploratory work is being continued.
6b) Indigenous barytes :- Work on the evaluation of the product has been completed.

# CHEMICAL ENGINEERING

## CE-1. POLYVINYL CHLORIDE
(January 1957)

Objective - Development of a process for production of PVC from chlorine and alcohol.

Pilot plant studies on the continuous production of EDC were continued, both for studying the various physical operations such as continuous washing, coalescing and separating the crude EDC subsequent to the reactor, and for the simultaneous preparation of the required quantities of EDC for studying its applications, such as thermal cracking to vinyl chloride, metal degreasing, and insecticide formulations. In all 103 runs were made, each varying from 1 hour to 53 hours and totalling to 295 hours, producing a total of 2250 lb. of crude EDC. Tech. pure EDC, satisfying the ISI specifications, was prepared. About 300 lb. of tech. pure EDC were sent to a local workshop for plant trials on degreasing of engine parts. The trials in their unit, originally designed for use with imported trichloroethylene, indicated that EDC can be satisfactorily used with some adjustments, thus saving appreciable amount of foreign exchange. further quantity of 410 lb. was sold to a firm manufacturing insecticides. A cost estimate was worked out for a 3 tons/day EDC plant.

The third stage, wherein the EDC is converted to vinyl chloride, by thermal cracking, presented new difficulties, partly due to the inherent nature of the process involving corrosion and choking of the reactor, and partly due to the existing external conditions such as the difficulties in ready procurement of suitable materials of construction for repair and modification of the reactor. Preliminary pilot plant runs on the vinyl chloride reactor had to be discontinued because of breakdowns and leakage, and repairs have not yet been possible on account of material shortage. In the intervening period, pending these repairs, alternative smaller reactors are being tried to obtain the monomer.

## CE-II. RAYON GRADE PULP
(August 1958)

Objective - To investigate the applied and fundamental aspects of the production of rayon grade pulps from indigenous cellulosic materials.

The investigations during 1959-60 pertained mainly to Dendrocalamus strictus, which is the most abundant variety of bamboo in India. The main attention was given to pulping by the water-prehydrolysis cum sulphate-digestion method on which 44 runs, each with 3 kg. of bamboo chips, were carried out under varying conditions. The chemical characteristics of the better pulps were acceptable, but the silica and iron contents were higher than desired. Their reactivities towards xanthation were found to be rather low.

The laboratory equipment fabricated in the NCL for viscose making and filterability evaluation was tested and standardized with imported pulps having known properties.

Survey by chemical analysis of the cellulosic raw materials was continued, and samples of Kardai, Arjun Sagda, groundnut husks and cashew-nut shells were analysed; similar work on spent lemon grass is in progress.

Most of the important units of equipment which are on order have not yet been received, but are expected shortly. Plans for the lay-out of the pilot plant in the new building have been drawn.

## CE-III. ISOPROPYL ALCOHOL
(April 1959)

Objective - To develop a process and to obtain design data for the production of isopropanol from acetone.

A catalyst was developed and tested in the previous year for the reduction of acetone to isopropyl alcohol by the Organic Chemistry Division. Data for the design of a commercial reactor using this catalyst are being collected. In the first instance the catalyst was tried in a bench-scale fluidized-bed reactor with a feed rate of about half-pound of acetone per hour, but was found unsatisfactory. Subsequently a fixed-bed reactor (2" diameter) was tried as an adiabatic reactor with satisfactory results. In all 14 runs, each of 3-4 hours duration, were carried out.. A continuous fixed-bed reactor, with an estimated capacity of about 5 lb. of isopropanol per hour, was designed and fabricated, and the integral equipment was assembled. Nineteen preliminary runs, each with 2 lb. of acetone feed per hour, were carried out. These indicated the need for some changes which have been effected, and eight runs of 4-6 hours each have been completed to study the performance of the unit.

Thermodynamic data were also compiled by calculation on this reaction. Liquid-vapour equilibria of the acetone-isopropanol system were determined experimentally at the normal atmospheric pressure in Poona (710 m.m.)

## CE-IV. ETHYL ACETOACETATE
(July 1958)

Objective - To develop a process for the manufacture of ethyl acetoacetate, an important organic intermediate, from indigenous raw materials.

This project, based entirely on the use of indigenous raw materials, consists of three principal steps : (1) the preparation of sodium ethoxide in a convenient form; (2) condensation of ethyl acetate in presence of sodium ethoxide; and (3) recovery and purification of materials for re-use.

Thirty experiments on a batch scale for the first step and ranging from about 75 g. to 600 g. sodium ethoxide have been carried out under different operating conditions. Consistent yields have been obtained under specified conditions. Certain improvements for reducing the time cycle are being tried.

Twenty experiments on the second step have been tried, using the ethoxide obtained above, to yield distilled, chemically pure ethylacetoacetate in quantities of 100 g. to 900 g. The overall theoretical efficiency of the whole process (Steps I and II) is encouraging, though further improvements are essential to increase the yields. Work has also been started on the recovery of ethyl acetate and its re-use.

## CE-V. HEXACHLOROETHANE
(June 1958)

Objective - To produce HCE by a direct, one-step catalytic process from ethylene and chlorine.

Investigations on the bench-scale single-tube monel metal reactor, with ½ lb. per hour capacity, using indigenous charcoal were completed by running it for more than 100 hours, during which about 50 lb. of good-quality hexachloroethane were obtained. Samples of this have also been approved by T.D.E.(M.E.), Kirkee. The catalyst showed a steady active life of nearly 100 hours, and the monel reactor and receiver did not show any particular signs of general corrosion. Subsequently, work on the testing of four Indian charcoals, including the active life of some, was carried out in a 500 cc. glass reactor. Of these, only one was found to be suitable for the reaction; two were inferior in conversion, the fourth had a rather short life. In addition, a fifth sample, representating a 500 lb. lot of the charcoal again supplied by the Aruvankadu Factory, was tested and found to be as satisfactory as their original two samples of 50 lb. and 70 lb. The five samples were also tested by analysis for various properties. Further, five different samples from reputed foreign manufacturers were compared with Aruvankadu charcoal in a 100 cc. glass reactor to determine the relative performance. It was observed that they gave similar results, except for one foreign sample which gave better conversions over a period of 12-15 hours; life tests on these were not carried out. The laboratory and bench-scale work on this project have been concluded, and a detailed report is being written up. A pilot plant has been designed and is being fabricated outside the NCL.

## CE-VI. ETHYLENE OXIDE
(March 1958)

Objective - To obtain process and design data for the production of ethylene chlorohydrin and ethylene oxide.

Increase in the output capacity of the 1" dia., 8½' high continuous glass reactor for ethylene chlorohydrin, maintaining practically similar conversion efficiencies as with previous lower outputs, was obtained by suitable modifications in the design of the reactor. Further, the effect of other operating variables on the performance of this reactor was also studied in 46 runs of 7 hours each. About 75 experiments, generally of about 5 hours duration, were also carried out on the 2½" dia., 9½' high continuous glass reactor, incorporating all the improved design features of the 1" dia. reactor, to confirm the results on the scale-up. Results were reproducible in the lower range space velocities tried till now. A pilot plant ethylene chlorohydrin reactor, about 5" i.d., and 10' high, has been fabricated in the NCL and has been sent out for rubber lining. An ethylene unit with a capacity of 10-15 lb. of ethylene per hour to feed chlorohydrin reactor will be fabricated.

About 55 laboratory experiments, using small quantities of the 5 per cent acidic ethylene chlorohydrin solution as obtained directly from the ethylene chlorohydrin reactor, have been carried out batchwise for the preparation of ethylene oxide. The conversions obtained (about 85 per cent on ethylene chlorohydrin) are satisfactory. The following quantities of ethylene chlorohydrin were also obtained during these investigations : (1) total ethylene chlorohydrin produced as 40 per cent from the 1" glass reactor, 25 lb.; (2) total ethylene chlorohydrin produced as 40 per cent from the 2½" glass reactor, 55 lb.; and (3) additional quantity of 5 per cent ethylene chlorohydrin solution (not further distilled) from both the reactors, 1500 lb.

## CE-VII. SORBITOL FROM GLUCOSE
(December 1957)

Objective -- To obtain process data for the high pressure catalytic reduction of glucose for production of sorbitol.

Work on the vertical stirred 2-litre autoclave was continued, and 25 further runs, each of 3 hours duration, have been completed, thus making a total of 49 useful runs on this equipment. This phase of the study for investigating the effect of different process variables with chemically pure glucose and Raney nickel is nearly complete. About 15 runs were also carried out in 5-litre autoclave with different stirrer design to test the scale-up conditions required for the design of this reactor. Arrangements for procurement of a larger batch autoclave and also a continuous reactor are being made.

## CE-VIII. PROCESS STUDY OF CATALYTIC HYDROGENOLYSIS - CETYL OCTADECYL ALCOHOL
(July 1959)

Objective - To work out a process for the production of a 50:50 mixture of cetyl ($C_{16}$) and stearyl ($C_{18}$) alcohols from indigenous raw materials for use in water reservoirs.

Preliminary bench-scale investigations on this reaction have been carried out in a 1.3-litre rocking autoclave, using distilled ethyl esters of cotton seed oil fatty acids to study the effect of different operating variables, and to find the approximate conditions for this reaction. Since cotton seed oil contains over 50 per cent excess of $C_{18}$ acid over that required to yield a 50:50 (weight basis) mixture of the final alcohols, it was considered desirable to process the feedstock to remove this excess prior to hydrogenolysis. Solvent extraction of the mixed glycerides and also of the mixture of ethyl esters of these fatty acids have been tried, but neither has been found to be useful for the purpose. Physical data, particularly on the vapour pressure of the ethyl esters, have been compiled from literature and by calculations for use in a distillation method of separating and upgrading the ester mixture.

## CE-IX. CARBON TETRACHLORIDE
(December 1958)

Objective - To develop a process for the production of carbon tetrachloride and chloroform from sewage gas methane in a fluidized reactor.

Laboratory scale investigations were carried out during 1952-54 on the chlorination of methane from sewage gas in a fluidized-bed glass reactor. Since considerable interest has been evinced in the utilization of sewage gas and also in the production of the two higher chlorinated methanes, including chloroform not covered in the earlier laboratory investigations, pilot plant work has been undertaken.

To begin with, a fluidized-bed reactor (4" i.d., 26" high) together with all accessories was installed. The whole unit is largely built from indigenous materials of construction and an indigenous catalyst is used. After 12 preliminary runs considerable improvements were made in the design and construction of the high-heat flux immersion heater which used to fail often in the early stages. Subsequently 28 regular runs, ranging from 1 hour to 12 hours of continuous operation, have been carried out to study the effect of some operating variables on the performance of the reactor; incidentally, about 75 lb. of distilled, tech. pure (I.S.I.) carbon tetrachloride have been obtained. An alternative design, incorporating external heating instead of internal immersion heating, will also be tried before a larger pilot reactor and a commercial reactor are designed. A glass laboratory fluidized-bed reactor 2" nom. i.d.; 42" high) of a similar design was also installed, particularly to carry out further detailed studies and for investigating the conditions for simultaneous production of chloroform. In addition to some preliminary runs, 47 systematic runs, ranging from 1 hour to 6 hours, have been carried out on this laboratory unit.

## PROJECTS TERMINATED OR CONCLUDED

(1) <u>Neem oil</u>

Work on this project was completed.

60-701

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(CONFIDENTIAL)

# NATIONAL CHEMICAL LABORATORY

## SUPPLEMENTARY NOTES ON THE ANNUAL REPORT

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# INORGANIC CHEMISTRY

## IC-I. CHEMISTRY OF RARE METALS

### (1) Studies in the isolation of pure rare earths

Experiments on the preparation of pure samaria by triphosphate (0.2% w/v) elution have been carried out with 6-9 g. oxide concentrate (30% $Sm_2 O_3$, rest mostly $Nd_2O_3$) loaded in 70 x 2 cm. dia. Dowex-50 (12x) columns. An advantage of the present method over EDTA method is that it is not necessary to convert the resin to a heavy metal form for the purpose of separation. The sodium triphosphate hexahydrate is prepared by a simple process developed in the laboratory in which trisodium phosphate is treated in solution with hydrochloric acid, followed by heating and crystallization under well-established conditions.

Of the other methods of resolution of the didymia-samaria mixture tried without much significant success, mention may be made of (i) sodium-amalgam reduction of samarium, (ii) fractional crystallization of magnesium double nitrate, (iii) solvent extraction with mixed amyl (fusel oil) phosphate and (iv) preferential extraction of the calcined mixed oxide. Ion-exchange fractionation into binaries gave better results and was, in fact, improved so as to give only two binary concentrates (Sm-Nd and Nd-Pr), with 50% recovery of Pr and 100% recovery of La in over 99% purity. Over twenty experiments on 100-120 x 5-6 cm. dia. Dowex 50 columns were run to standardize conditions for obtaining the binary Sm-Nd and Nd-Pr concentrates, average load per column being about 90-120 g. mixed oxide. It is proposed to step up the scale by a factor of ten, to collect sufficient concentrates for further purification as also to test the large-scale workability of a strong cation-exchanger (sulphonated styrene) prepared in the Polymer Chemistry Division.

The Manager of M/s. Chunilal Ootamchand and Co., Bombay, visited this Laboratory in January and submitted a proposal in Fabruary 1960 stating that his firm, which has ready clients for rare metal oxides, wants exclusive agency for the sale fof the pure oxides of the following metals prepared in the NCL. : Zr, Hf, Nb, Ta, La, Ce, Pr, Nd and Sm. The price which his firm offered was the rate of Johnson, Matthey & Co. enhanced by 40%. The preparation of some of these high-purity oxides for research purpose (Zr, Hf, Nb, Ta) is subject to A.E.C.'s releasing of scheduled minerals zircon and tantalo-columbite in appropriate quantities. Also, a substantial part of the research carried out in the NCL on the preparation of the pure oxides especially the rare earths (La, Ce, Pr, Nd, Sm) was supported financially by the Department. The matter has therefore been referred to the Department of Atomic Energy for its views.

### (2) Separation of zirconium from hafnium

The methanolic effluent, after recovery by distillation, contains over 1.5% v/v of water, which seriously interferes in subsequent elution. Of the several methods used for its removal viz., treatment with calcium oxide, caustic alkali, magnesium etc., the simplest process of fractionation was preferred and standardized to give a recovered solvent containing below 0.5% of moisture. Its usability has been completely established in running a battery of four columns, in which the solvent was recycled in succession.

Reactivation of the gel is not difficult, but complete removal of the two metals, particularly hafnium, from the used gel posed a difficult problem. Leaching at an appropriate stage with moderately dilute sulphuric acid at room temperature appears to the best solution found so far. More experiments will be necessary to establish optimum conditions and repeated use of the acid over several extractions.

Basic data were collected from 110 x 7 cm. dia. silica gel columns (2 kg. of gel) which handles, on the average, 550 g. of natural oxide in a 1.5% methanolic solution (as oxychloride hydrate) over a period of about four weeks, including all stages. Yield of fractions (% oxide equivalent) : pure zirconia 70-75 (Hf/Zr $<$ 0.01%), low-hafnia zirconia 25-20 (Hf/Zr about 0.5%), hafnia concentrate 5 (Hf/Zr $>$ 20%).

Twenty-five solvents were examined for the determination of extractive separation factor of zirconium and hafnium, starting with the natural mixture from Indian zircon. The value ranges from 1.0 to 6.2. TBP, a current solvent of choice, has been reported to be used under conditions where this factor is about 10.

Methyl propyl ketone at low temperature, amyl alcohol, ether, ethyl and amyl acetates offer good possibilities as a multi-stage extractant from nitric acid medium, especially in presence of a salting out agent like calcium nitrate.

### (3) Separation of niobium from tantalum

The new solvent extraction process, on which a detailed flow-sheet with explanatory notes was sent in September 1959 to Dr. J. Shankar, Head of the Chemistry Division, A.E.E., Bombay, used methyl propyl ketone as the extractant, a by-product of the acetone plant of M/s.Sirsilk Ltd., Sirpur-Kaghaznagar. The Company was interested to know if the product would be useful to this Laboratory, and sent a sample in June, 1959, mentioning that they were then holding a stock of 2 tons of this ketone. In a two-step batch extraction cycle, the process gives niobium and tantalum oxides, each contaminated with less than 0.03% of the other from a mixed oxide in which they are present in the weight ratio of about 2 : 1.

## IC-II. PREPARATION OF SPECIAL INORGANIC CHEMICALS

### (1) Sodium hydride

The conversion of metallic sodium dispersion by the pressure hydrogenation method was 85-95%. The product of reaction of sodium hydride and methyl borate is a mixture of sodium borohydride and sodium methylate, from which the borohydride was obtained in 90% purity by a single extraction with isopropylamine.Further purification is being carried out.

## (2) Fluorescent zinc sulphide

The green phosphor was prepared by mixing a slurry of pure zinc sulphide, freshly prepared, with 0.01 per cent of copper chloride and 2% of sodium chloride, drying and calcining in nitrogen at 880°. A sample was duly approved by the Defence Establishment before the larger lot was prepared and supplied at Rs.80.00 per lb.

## (3) Oxides for semiconductors

Processes for the preparation of high-purity oxides of manganese and nickel have been developed and standardized. Others are under investigation.

## (4) Soda-lime granules for hospitals

50 g. samples of our material was supplied to Miss Joel Bishop, Nurse Adviser, TCM, who had brought up this proposal. Hospital trial reports are awaited from her. In the meantime, a total of 3 lb. of the soda-lime has been prepared.

## (5) Titanium organics

A total of 15 lb. of the varnish has been prepared and supplied to four parties in the last six months. A flow-sheet prepared for the Industrial Liaison Officer, Madras Circle,in 1959 shows economic feasibility of the process on the basis of laboratory data.

## IC-III. EXPERIMENTS ON INDIAN BARYTES

To examine the economics of our acid-leaching process for the treatment of the two off-coloured barytes sample sent by Andhra State Government for our study, information was sought on the estimated maximum expense allowable for bleaching per unit weight of the substandard material in April 1959. A sample of the grade approved as marketable was also asked for. Reply has not been received from the State Government in spite of reminders.

Over fifty experiments on chlorination have been carried out with briquettes (180 g.) made from 100 g. mineral. An interesting feature of the experiment that, though chlorine is used in excess of 30% over the theoretical, there is little loss of chlorine as such, indicating formation of volatile chlorinated products. The composition of the mixed exit gases is being examined.

Average conversion of barium sulphate to chloride is 85-90 %, which compares very favourably with the two-step carbon-reduction process. Sulphurous gases may provide useful by-products. Conversion of chloride to nitrate is 80 % or over with equivalent amounts of reactants.

## IC-IV. CATALYTIC OXIDATION OF SULPHUR DIOXIDE TO TRIOXIDE

About 30 experiments (in duplicate) have been carried out at space velocities ranging 80-925 litres/litre of catalyst/hr. with two industrial fresh catalyst samples, one spent sample, nine synthetic potash-vanadium-silica gel samples and one regenerated industrial sample. Conversions ranged from 95 to 98 % (except for samples containing high proportions of tetravalent vanadium) as measured by Reich test. The Reich test consists in passing the mixture of gases (after scrubbing out $SO_3$ where necessary in $SO_2$-saturated sulphuric acid) into standard excess iodine solution for a specified time and titrating the excess of iodine with standard thiosulphate. The gas mixture is preheated electrically to about $300^o$, where it enters the catalyst bed, in which is centrally embedded a chromel-alumel thermocouple for measurement of catalyst bed temperatures. Catalyst is used generally in the form of cylindrical pellets 9 mm x 8 mm dia. approx., prepared manually with a small pellet press, but for high velocities 8-10 mesh granules were used by screening the partially dried catalyst as such. Approximate composition of catalysts; $V_2O_5$ (total) 6-9, $K_2O$ 5-6, $SO_3$ 15-20, $SiO_2$ 57-67 per cent (rest water).

## IC-V. ANALYTICAL RESEARCH AND SERVICE

Analytical service work carried out during the year included the following major items :

(1) About 500 samples of $ZrO_2$ and $HfO_2$ for spectrographic estimation of Hf and Zr contents respectively.

(2) About 100 samples of $Nb_2O_5$ and $Ta_2O_5$ for Ta and Nb respectively.

(3) Twelve samples of kiln dust and one sample of fly ash (from boilers) from A.C.C. cement factories for flame photometric estimation of lithium contents; in only three kiln dusts, lithium was detectable, concentration being 0.01-0.02 %.

(4) A sample of titaniferous iron ore from Director of Industries, Bombay, for the estimation of titanium and vanadium contents; $TiO_2$ 14.7, $V_2O_5$ 1.07 per cent.

Polarographic study of complex formation of sodium triphosphate with heavy metals is pursued as a subject of fundamental analytical interest. Using a derivative circuit, it has been found possible to estimate niobium ($E = -1.6$ V Vs. S.C.E.) in presence of tantalum in a triphosphate medium.

## MISCELLANEOUS WORK

### (1) Rutile $TiO_2$ pigment from bauxite sludge

Studies on upgrading and chlorination, followed by hydrolysis and calcination were completed on laboratory scale (1-3 lb. of sludge) with sludges received from both the aluminium companies, Aluminium Corporation of India ($TiO_2$ 23%, $Fe_2O_3$ 14%, $Al_2O_3$ 34%, rest $SiO_2$, volatiles, $Na_2O$) and the Indian Aluminium Company ($TiO_2$ 27%, $Fe_2O_3$ 23%, $Al_2O_3$ 19%, rest $SiO_2$, volatiles, $Na_2O$ and $CaO$). In both cases, the acid obtained at the hydrolysis stage was found sufficient to upgrade a corresponding amount of sludge by dissolving out iron oxide and a portion of alumina. Chlorination of the residues (39% and 49.5% $TiO_2$ respectively) in the temperature range 400-500°, showed preferential chlorination for $TiO_2$, 75-80% of which was collected as brown liquid ($TiCl_4$) in the condensers. A clarification process of the tetrachloride without involving distillation, yet giving a product suitable for hydrolysis to white titanic acid was worked out. Suitable conditions for hydrolysis below 60° (to enable the use of rubber-lined vessels), conditioning agents, calcination and grinding were also worked out on laboratory scale (125 to 250 g. $TiO_2$).

A full report is being prepared for submission to the Scientific Advisory Committee.

### (2) Synthetic cryolite

The work was concluded and a full report submitted in the first half of the year under review. Only two methods of solubilizing fluorine from fluorspar were investigated. The first one, namely preferential dissolution of fluorspar in an aluminium sulphate solution, has the merit of excluding silica and has special significance in view of the highly siliceous character of the Madhya Pradesh (fluorspar) deposits. But the method did not work well, the special difficulty being to precipitate cryolite (without heavy contamination by alumina) from the aluminium fluorosulphate solution. The second method was extraction by alkali fusion, for which ilmenite was found to be a good catalyst. The extract contained much silica with the fluoride, and a method of removing the soluble silica was worked out. Finally, cryolite of good quality was obtained from the silica-free sodium fluoride solution. The process is technically feasible but is not economically competitive at the present prices of raw materials.

### (3) Short-term problems

(a) Removal of iron from caustic lyes used in the rayon-grade pulp project of NCL - A simple process depending on surface adsorption of the colloidal ferric hydroxide on a crystalline lattice was worked out.

(b) Ceria glass-polishing powder - A product meetin- the requirement of a local manufacturer of compound optical lenses was prepared. The party is also interested in alumina abrasive and is keeping close touch with the work of the Laboratory.

## (4) Reports

A research report on "Studies on the preparation of aluminium-grade cryolite from Indian fluorspar (siliceous)" was submitted to the Secretary, CSIR, New Delhi, in September 1959.

## (5) Patents

Complete specification in respect of Patent Application No.67513 for "Improvements in or relating to the separation of niobium and tantalum from each other by liquid-liquid extraction" has been sent to the Patents Officer, CSIR, for filing.

# POLYMER CHEMISTRY

## P-1. FUNDAMENTAL STUDIES IN HIGH POLYMERS

### (1) Low polymers of ethylene

The aim of the undertaking is to synthesise the alkyl component of surfactants of the alkyl aryl sulfonate type or superior in properties to the imported products available in the market at present. The synthesis is based on the raw materials easily available in the country viz., ethylene from alcohol. Laboratory work is in progress to standardise the procedure for obtaining the low polymers of ethylene viz., hexamers for further alkylation reaction with benzene. The difficulties experienced in alkylation of the hexamers are probably due to the inhibitory effect of various side reaction products formed during the polymerisation of ethylene and emphasis is now laid on the purification of the polymer prior to alkylation. The alkylation reaction study involves a detailed investigation of various catalyst systems and other related factors.

### (2) Polymerisation

The production of graft copolymers from natural rubber using vinyl compounds has been of considerable interest recently due to improved properties of graft copolymer vulcanizates. The main difficulties encountered in attempts in polymerising vinyl monomers in presence of ammoniated latex are on the retarding influence of rubber on vinyl polymerisation and the sensitiveness of the initiating system to ammonia present in latex. The redox system developed in the Laboratory is insensitive to ammonia and can be worked at room temperature. A process has been developed for the graft-polymerisation of methyl methacrylate with natural latex and the graft copolymer vulcanizates were found to have substantial enhancement of mechanical properties like tensile strength, abrasion resistance and shore hardness in comparison with natural rubber vulcanizates. Test reports on its performance are awaited from the industry, to whom sample has been sent.

### (3) Solution properties

The nature of extrapolation curves (of viscosity vs conc. plots.) at very high dilutions ($<0.1\%$) of polymers has been the subject of intensive study during the last few years. The object has been to determine the nature and cuase of the discontinuities, if any, in such curves. Studies carried out in this Laboratory showed that configurational changes of macromolecules at high dilutions are responsible for the maxima, minima effects observed in very dilute solution behaviour of polymers, though in special cases e.g. polymethyl acrylate the alternate cause, namely adsorption of the polymer molecules on the walls of the capillary may be of considerable importance. These investigations aim at a better understanding of the behaviour of macromolecules in solutions.

Systematic investigations on the behaviour of polymer molecules in binary mixtures of solvents and non-solvents have led to a more advantageous one-parameter molecular weight determination of polymers. The method is being subjected to intensive experimental verification.

## P-2. ION EXCHANGE

Ion-exchange technique is finding greater and wider application in recent times. This has resulted due partly to the availability of different ion-exchange materials with superior qualities applicable either to special problems or with a wide range of properties. Work in this regard has been broadly divided into two aspects viz. (1) synthesis of different types of ion-exchange resins and membranes from indigenously available raw materials wherever possible and (2) applications of resins and membranes for specific problems such as water softening, demineralisation, electrodialysis, purification and recovery of organic compounds etc.

### (1) Synthesis of resins

Cation-exchange resins - A method of preparing a cation-exchange resin based on commercially available cashew-nut shell liquid has been successfully studied on a pilot plant scale and the process handed over to industry by NRDC.

A technique for preparing cation-exchange resin based on styrene-divinyl benzene polymer has been worked out. Semi-large scale preparation has been successfully completed. Such resins have high capacity and exhibit a better performance than the commercial phenolic type resins.

Anion-exchange resins - Melamine-formaldehyde reaction product and polyvinyl chloride-pyridine reaction product have been prepared on semi-large scale and the products are being tested.

### (2) Membranes

Besides preparing the ion-exchange materials in the resinous form it is also possible to prepare them in sheet forms. This is possible in two ways viz., (1) Homogeneous membranes, where the reaction product yielding the ion-exchange material is cast in the form of sheets, rods etc. without any mechanical support and (2) Heterogeneous membranes, where already available ion-exchange resins are ground to a fine form and intimately mixed with an inert binder such as polyethylene etc. and cast or rolled in the form of sheets in conventional equipment. Work has been carried out by preparing homogeneous membranes in a small scale for studies on Donnan diffusion and heterogenous membranes are being prepared based on rubber latex and available CNSL Cation-exchange resin and other resins.

### (3) Applications

(a) Water softening - The cation-exchange resin prepared from CNSL is being used in the sodium form for treating boiler feed water in the Laboratory and in many commercial installations.

(b) Water demineralisation - The CNSL cation-exchange resin in combination with locally prepared anion-exchange resins is being studied for reducing the salt content of different types of waters.

(c) Electrodialysis - Using membranes in an electrodialysis cell it is possible to separate cations or anions from each other under an applied potential and study degree of removal of salt under different conditions such as variation in rate of flow, variation of potential etc. etc. A small cell assembly has been constructed for conducting various studies.

## P-III. RUBBER

### (1) Rubber base adhesives

A series of phenolic resins were prepared under various conditions (molar ratio, pH, etc.) and mixed with compounds of Chemigum N7, containing various fillers and curing ingredients. Steps were taken to standardise all stages viz., preparation of the resin, making of the rubber compound, mixing the resin and the rubber, storage stability of the adhesive and its consistency preparation of the surface of adherends, application of the adhesive, its thickness, drying time, assembly, heat curing, ageing, room temperature bonding and testing. The maximum breaking load recorded for steel in shear was 2225 p.s.i., the average figure being 1700 - 2000 p.s.i. For the same adhesive, steel gave higher values than aluminium; many of the latter failed in the metal and not in the adhesive. Chemigum N5 and N600 were tried, using modified formulations. Room temperature bonding was carried out with leather, cured nitrile and natural rubbers, canvas, steel and aluminium, with our own formulation as well as Goodyear's 'Pliobond', under idential conditions, according to ASTM D-816-55. Our formulations compares favourably with 'Pliobond'. The shelf-life of our adhesive, however, is only about 3 weeks and this has to be considerably improved.

### (2) Microcellular rubber

A new blowing agent based on urea derivatives, (Ind. Pat. 69620) already developed at NCL, was studied in detail. 1/2 to 1 lb. samples were tested in industry and gave promising results, larger amounts upto 5 lb. were later supplied for further trials, and final reports are awaited. A comparative study of BL-3 and vulcacel BN was undertaken. Specific formulations (designed for mechanical use) based on natural rubber and Butyl rubber were taken up first. Mixing, curing and testing were carried out under idential conditions, according to ASTM-1056-50T. Data were collected on specific gravity and compression set at constant deflection. The samples, however, were discs of 1" dia. instead of 1.129" as specified. The compound developed here compares favourably with Vulcacel BN.

## (3) Identification of antioxidants, antiozonants and copper inhibitors

The object is to develop simple methods of identifying common commercial antioxidants in original form or in rubber compounds, uncured, cured and aged. Investigations were carried out with ten commercial antioxidants suggested by the industry. Tests were based on reactions with a series of oxidising agents and also with different diazotised amines at different pH values. These reactions give different colour patterns by which the above antioxidants could be identified. As a supplementary evidence paper chromatographic studies were carried out with different mobile phases and developing agents according to Zipp's method and the characteristic colour of the spots and their Rf values were noted.

## (4) Processing of indigenous China clays

Eight Indian clays were studied - Kendposi (Bihar), Bhonda (Bihar), Appenhalli (Mysore), Nandihali (Mysore), Thirthahalli (Mysore), Kannapuram (Kerala), Palyangadi (Kerala and Rairangpur (Orissa). Four of these from Kendposi, Bhonda, Palyangadi, and Kannapuram were processed as follows: They were subjected to high speeds stirring in presence of water and dispersing agents, passed through 250 mesh sieve, centrifuged, filtered, dried, pulverised and evaluated in natural rubber. Untreated clays were compounded similarly for comparison. Tests were made on Mooney viscosity, Mooney scorch, tensile properties, tear resistance, shore hardness, abrasion resistance, specific gravity, ignition loss, oil adsorption, moisture content and brightness. For Kannapuram clay, the tensile strength was found to rise from 1890 (untreated) to 3200 p.s.i. (washed). The imported Suprex clay gave a tensile strength of 3400 p.s.i.

All the eight clays were studied for particle size distribution. Suprex was used for comparison. Clays from Palyangadi, Kannapuram and Thirthahalli show a high promise of being good reinforcing clays after proper refining.

Traces of talc were observed to bring about a marked change in the column height in a sedimentation experiment on pure Kaolin-clay like Suprex. To investigate whether these traces caused the formation of the aggregates of Kaolinite particles, a mixture of 90% Suprex and 10% Talc was prepared and various fractions were collected from it (for DTA study) by sedimenting the mixture in water under varying physico-chemical conditions. The fractions were dried at $105^{\circ}$.

To process the clays further an air flotation unit was prepared and set up. Quantitative work on large scale washing is in progress. Electron microscopic work on the two new samples received viz. Palyangadi (Little special) and Kundara (unprocessed) has been undertaken.

## P-IV. INDUSTRIAL POLYMERS

### (1) Polystyrene

The technique of suspension polymerisation developed earlier in the Laboratory has certain advantages over the bulk polymerisation method adopted by the Polystyrene Factory at Bombay. The product is obtained in the form of small spheres.

The technique has been extended for copolymerisation of styrene with divinyl benzene for producing a suitable matrix (in the form of spherical particles) for preparing cation-exchange resins.

The technique is also being extended for the preparation of expanded polymers by incorporating a suitable blowing agent during polymerisation.

## P-V. FOLLOWING PROCESSES DEVELOPED IN THE DIVISION HAVE BEEN RELEASED FOR COMMERCIAL EXPLOITATION

1) Foundary core oil. - Released free of cost.

2) Factice from Tobacco seed oil. - Released free of cost.

3) Can-sealing composition. - M/s. Arya Chemical Works, Calcutta.

4) Pressure sensitive adhesive tapes. - M/s. Andandilal Hemraj, Bombay.

5) Cation-exchange resin from commercial cashew nut shell liquid. - M/s. Tulsi Industries, Poona.

6) Enamels for bobbins. - M/s. Raghunath Enamels Ltd., Kanpur.

# CHEMICAL ENGINEERING

## I. POLYVINYL CHLORIDE

### (1) Ethylene and EDC Plants

In the pilot plant studies, the rate of production of EDC varied from 6 to 11 lb. per hour, the average being about 7.7 lb. per hour. EDC hold-up in the reactor in these runs was 97 lb.

Conversion of chlorine to chlorinated products ranged from 95 - 100% at chlorine rates of .08 to 0.09 mols per hour at this hold up which corresponds to an approximate output of 8-9 lb. of crude EDC per hour. Chlorine conversion gradually decreased to about 85% with a gradual increase to about 20% in the chlorine flow rate. Ethylene in the feed was in 5-10% excess of the theoretical; this was necessary for obtaining almost complete conversion of chlorine at the optimum space velocity. No particular advantage was observed by increasing the proportion of ethylene in feed beyond this.

During the long runs the crude EDC produced was continuously washed with 6% NaOH solution in the washer and the mixture was passed through the coalescer. Clear washed EDC was obtained from the coalescer. Proportion of EDC to caustic liquor was kept at 1:1 by volume and this ratio was found suitable to reduce the chlorine content in crude to less than 0.00003% and acidity to about 0.004%.

The crude EDC contained 85-95% EDC (satisfying ISI Specification). A sample of the higher chlorinated products was separated into several fractions by distillation under vacuum and these fractions are being analysed for carbon, hydrogen and chlorine.

### (2) Vinyl Chloride Plant

Eight preliminary runs, each of about 2-3 hours duration, preceded by 5-6 hours of heating-up period, were carried out in the pilot plant reactor. Vinyl chloride gas was obtained at the rate of about 5-6 lb /hour. In subsequent runs, the rate gradually decreased due to considerable choking resulting in enormous back pressure. The reactor was dismantled and examined; the tubes were found choked and partly corroded. The reactor is being repaired.

Twenty-six runs of 1-6 hours duration were carried out in a smaller electrically heated packed reactor to collect vinyl chloride gas. The temperature ranged from 460 - 490°. The quality of the gas, however, varied in different experiments. The reasons for this are being investigated.

## II. RAYON GRADE PULP

Dendrocalamus strictus is the most abundant variety of bamboo in India. Next in order is Bambusa arundinacea which, however, is available in much smaller quantities than the former, and largely in Maharashtra and Mysore States.

Investigations on the latter are also proposed to be undertaken in due course.

The first step of pulping consisted of water prehydrolysis, the conditions of which were optimised for a pentosan reduction to 2-3% in the final pulp. The maximum temperature of prehydrolysis was 170° at which neither was there any disproportionate increase of lignin nor any undue loss of alpha-cellulose. However, the prehydrolysis made the linkages in cellulose more liable to degradation in the subsequent alkaline cook.

The optimum conditions of the sulphate cook, subsequent to the prehydrolysis, were 2 hours at 170° with 18.75% $Na_2O$ as total chemicals.

The unbleached pulps were bleached by multi-stage sequence using elemental chlorine and sodium chlorite. The bleached pulps, on an average of 12 experiments, had the following properties: alpha-cellulose - 95.3%, ash - 0.33%, silica - 0.054% and viscosity - 8.0 cp. (C.E.D.) at an average yield of 30.6%.

To evaluate the bleached pulps, laboratory equipment such as shredder, xanthation churn, and filterability blow case etc. were fabricated in the NCL Workshop according to standard designs for use till the receipt of the integrated Emil Blaschke unit. Some of the bleached pulps were then evaluated for viscose making and filterability by standard methods and were found to be rather low in their reactivity towards xanthation.

In an effort to understand the chemical nature of some cellulosic raw materials, chemical analysis for the main constituents, such as lignin, cellulose, hemicelluloses and extractives, was carried out for the following raw materials: 1) cashew nut shells, 2) Kardai, 3) Arjun Sagda seeds and 4) groundnut husks. The results, in general, showed variation of $\alpha$-cellulose (from holocellulose) from 25 to 35 per cent and having a D.P. in the range of 1000-1200. The lignin content varied from 12 to 28 per cent and the pentosan content from 10 to 20 per cent.

## III. ISOPROPYL ALCOHOL

The laboratory fluidized bed reactor (2" dia. glass) was used with 500 c.c. (320 g.) of katalyst (-70, + 150 mesh). The main observation in the working of this reactor was the susceptibility of the catalyst to crumble and form a fine powder thereby causing heavy losses due to entrainment in the outgoing gases. Similar failure due to crumbling was also noted even when a larger size (-36, + 72 mesh) was used. About six runs were tried under these conditions, without any satisfactory result. It was hence felt that due to this performance of the particular catalyst, the fluidized reactor, which would have been probably otherwise helpful in dissipating the heat of reaction, is not suitable.

Experiments in a static bed, were next carried out in a 2" dia. glass column. A similar volume of the catalyst (500 c.c. wt. 310 g. and -12, + 20 mesh size) was used. Eight experiments were carried out and 70-75% conversion per pass was obtained.

Based on these results, a pilot plant designed to produce about 5 lb. of isopropyl alcohol per hour was fabricated and installed. Preliminary experiments were first carried out with a feed rate of 2 lb. of acetone per hour, using the catalyst (volume 250 c.c., wt. 1,500 g. and ¼" size). Certain modifications of the equipment were carried out based on the observations in the preliminary experiments. In order to minimize any likely channeling of the gases, with the original cubes of the catalyst, it was considered preferable to use regular circular pellets 3/8" dia. prepared in a tableting machine. Eight experiments have been carried out using this catalyst and the results showed an average conversion from 60 - 67% of isopropyl alcohol at a feed rate of 2 lb. of acetone per hour and using a 1:3 ratio of acetone to hydrogen as in all the earlier experiments.

## IV. ETHYLACETO ACETATE

The first step essentially consists of the ternary azeotropic process using benzene for the continuous removal of water of reaction between sodium hydroxide and ethanol. The two different principal variables studied were the height of the column and the ratio of benzene to the reactants in reactor, the other factors such as the reflux ratio, the ratio of ethanol to NaOH, rate of boiling etc. being maintained nearly constant in all the runs. Though the initial runs were discontinuous, necessary modifications of equipment were later made to enable continuous operation for each run and also the regular continuous feed-back of the benzene-layer after the automatic separation of the ternary. Consistent yields of 91-92% conversion of NaOH to sodium ethoxide were obtained in 10 experiments ranging from an initial charge of 200 g. to 400 g. of NaOH, after all the variables were standardized. However, it was observed that the period necessary to obtain the above conversion was too high and increased with the increase in the charge. Attempts to rectify this are being made.

The condensation was studied essentially keeping the molar ratio of the two reactants - sodium ethoxide and ethyl acetate - constant (1:2) in all these runs. The optimum quantity of addition of ethyl acetate required for the removal of ethanol, a product of reaction, as the binary azeotrope was arrived at after some investigations for the present set-up of the equipment. The conversions were about 75-76% on the exhoxide, thereby giving an overall conversion of 68-69% on the original NaOH used.

## V. HEXACHLOROETHANE

### (1) Work with single tube monel metal reac capacity

Cupric chloride impregnated activated c charcoal was used as the catalyst, at circa 250° excess of chlorine over the theoretical at the op velocity.

The hexachloroethane obtained was a free flo white crystalline solid which appeared to be somewhat than that from the large glass reactor. The active li the catalyst was also found to be about 1½ times that in large glass reactor.

### (2) Testing of activated charcoals

(a) From Indian firms/institutions - Two samples, viz. "Hykole X" and "Hykole O" from R.R. Laboratory, Hyderabad, one from M/s. Narbada Valley Chemical Co., Rajpipla, and one from M/s. Techno Chemical Industries, Kozhikode, were tested. "Hykole O" and the sample from M/s. Techno Chemical Industries were quite inferior since they yielded only a liquid product even with a fresh sample. The sample from M/s. Narbada Valley Chemical Co., Rajpipla, had only half the active life when compared with that of Aruvankadu charcoal, under similar conditions. "Hykole X" gave conversions similar to that obtained with Aruvankadu charcoal, and in addition it had a longer active life, by about 1½ times, and was therefore found to be suitable for our purpose.

(b) Foreign activated carbons - The five samples were (i) RKD II extra from M/s. N.V. Norit Co., (ii) Anticarbone 4MB 10/12 mesh size from M/s. British Ceca Co., (iii) No.203 Type B 10/12 mesh from M/s. Sutcliff Speakman Co., (iv) Grade ACC Columbia activated carbon 6/14 from M/s. National Carbon Co., (v) BPL 10x14 mesh from M/s. Pittsburgh Coke and Chemical Co.

These were tested only for brief periods of 10 to 15 hours. While they all gave conversions of the same order as with Aruvankadu charcoal, sample No.203 type B from M/s. Sutcliff Speakman gave even higher conversion approaching nearly 100%.

## VI. ETHYLENE OXIDE

Further experiments were carried out on the 1" dia. glass reactor with a feed rate of 95.5 g. of chlorine per hour and equivalent quantities of other reactants to confirm the reproducibility of the earlier results, and to simultaneously obtain the 40% azeotrope after distillation for further use. Conversions of 84-88% were obtained as before. To study the effect of still higher space velocity on conversion, further experiments were carried out in the same reactor with a feed rate of 122.8 of chlorine per hour maintaining the ratio of ethylene and water to chlorine as before. Conversions fell down to 75%. Subsequently the

placed by finer pore size sintered
conversions as high as 85% could be
at the latter feed rate. This was
p to 131.6 and 149.9 g. of chlorine per hour,
ing conversions of 83 and 77% respectively
The effect of packing, with glass raschig
dia., was studied, but no significant effect
erved.

periments were further continued on the 1" glass
o study the effect of ethylene chlorohydrin
ation on conversion efficiency by adjusting the water
At 6.3% concentration, no particular effect on the
rsion efficiency was noticeable while further increase
e concentration resulted in a drop to 72%. Considerably
ased quantities of EDC, formed in the latter cases by
t combination of ethylene and chlorine, separated as
ganic layer. This also caused increased heat output,
appreciably raised the temperature of the reactor
reby affecting the main reaction unfavourably.

The 5% solution was used in the next step viz. dehydrochlorination of ethylene chlorohydrin to yield ethylene oxide. This was prepared in several preliminary experiments by adding 2 litres of ethylene chlorohydrin dropwise to a boiling solution of $Ca(OH)_2$ under stirring at about 98°. The vapours were chilled to below 5° in a copper spiral condenser to try and condense the water vapour and ethylene oxide together However, it was not quite possible to quantitatively condense the same. A series of further experiments were then done to separate the oxide and the water vapour by using a partial condenser for water and then condensing the ethylene oxide vapours, but even in this case the nearly anhydrous ethylene oxide could not be obtained.

With a view to determining approximately the conversions obtained in this step, various known quantities of ethylene chlorohydrin and $Ca(OH)_2$, the latter always in 10% excess, were boiled and ethylene oxide was absorbed in a $CaCl_2$-HCl mixture as fast as it was issued out. The approximate conversions so obtained were about 85-90%.

## VII. SORBITOL FROM GLUCOSE

In the 19 runs on the 2-litre vertical stirred autoclave the variables studied were hydrogen pressure (175 to 575 psig.), initial glucose concentration (24.4 to 54.2% glucose), ethyl alcohol-water mixture as a reaction medium (0 to 80% ethyl alcohol) and stirrer speed (200 to 600 r.p.m.). Results indicate that the conversion depends both on pressure and on stirrer speed. A threefold increase in stirrer speed nearly doubles the conversion, while a similar increase in pressure increased the conversion by about one and half times. It was also observed that the alcoholic solutions are more easily hydrogenated than the aqueous solutions. The conversions, in the range of concentration studied, are almost independent of the initial glucose concentration. Activity of the catalyst for repeated use, without activation, was studied and six runs were carried out using the same