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## BIOCHEMISTRY DIVISION

### I. CITRIC ACID FERMENTATION

#### (a) Carbohydrate metabolism in *Aspergillus niger*

1. Aldolase from *A.niger* and from other fungi was found to be a metallo-protein which was inhibited by metal chelating agents and reactivated by zinc.

*A.niger* aldolase was purified about a 100-fold by alkaline ammonium sulphate fractionation followed by selective adsorption on calcium phosphate gel and elution with concentrated ammonium sulphate solutions. The final preparation had a specific activity of 40 units per mg and was electrophoretically homogeneous at two different pHs. The enzyme was free from other glycolytic enzymes. It contained zinc but no iron or manganese. The inhibition of the enzyme by metal chelating agents could be reversed by divalent Zn, Fe, Co or Mn but not by Cu, Ca, Mg, etc.

Phosphohexoisomerase of *A.niger* was obtained in a state of high purity. It was found to require no co-factors or metals for its activity.

2. Zwischenferment from *A.niger* was isolated in good yield with a high specific activity comparable to that of the enzyme from yeast. It was free from other interfering enzymes and has been used for the rapid analytical estimation of several enzymes, glucose-6-phosphate, ATP, co-enzyme II, etc.

#### (b) Role of carbon dioxide in citric acid production by *A.niger*

##### (i) CO<sub>2</sub> fixation and citric acid production

In experiments with radioactive C<sup>14</sup>O<sub>2</sub> it was found that the higher the yield of citric acid the higher was the incorporation of atmospheric CO<sub>2</sub> in the citrate. When a yield of 70% was obtained, as much as 7-14% of the citrate carbon was derived from the atmospheric CO<sub>2</sub>. The incorporation was small

in the initial stages of the fermentation but reached higher proportions in the later stages when citrate was being actively formed.

Radioactivity was found to be incorporated only into the carboxyl carbons of citric acid isolated in these experiments; the distribution of radioactivity in the primary and tertiary carboxyls was slightly greater than 1, indicating that a large degree of equilibration takes place among the four carbon dicarboxylic acids before they are condensed into citrate.

(c) Influence of CO<sub>2</sub> tension on citric acid production

Excess CO<sub>2</sub> initially present in the atmosphere over a fermenting culture of A.niger greatly influences the rate of citric acid production. Growth of the mould and the rate of citric acid production were greatly accelerated with 0.1 to 0.5% CO<sub>2</sub> in the atmosphere, whereas concentrations of CO<sub>2</sub> over 1% had a slight retarding effect. This effect of excess of CO<sub>2</sub> was observed with cultures in flasks as well as in small glass dishes, with glucose as substrate. Experiments with commercial sugar as substrate are in progress.

(d) Trace elements in citric acid fermentation

Citric acid yields were decreased when excessive iron was present in the medium, but the effect of iron was reversed by the addition of zinc. With commercial sugar as substrate the optimum levels of these elements were found to range between 248-351 µg Fe<sup>+++</sup> and 114-171 µg Zn<sup>++</sup> per litre of the medium, giving yields of 80-85% citric acid in 7-8 days.

In experiments with A.R. sucrose a much lower optimum was observed for these two elements; but the fermentation however took longer time.

## II. BIOSYNTHESIS OF RIBOFLAVIN

Cultural studies of the fungi Erethothecium ashbyii and Ashbya gossypii with strains available in the Laboratory were

undertaken, the cultures purified and a high riboflavin-yielding strain of E. ashbyii isolated.

### III. ENZYMES

#### (a) Proteases of bacillus licheniformis

Further purification of the protease from Bacillus licheniformis has been carried out. The crude enzyme concentrate was freed of mucilaginous matter and fractionally precipitated with cold acetone into proteinase and peptidase fractions. The proteinase was further purified by repeated precipitations with ammonium sulphate and cold acetone. The purest preparation had a specific activity of 2.9. Analysis by free flow electrophoresis at three different pHs showed a major active component and a minor (5% of total) fast moving inactive fraction. The purification of the same protein has also been effected by electrophoresis on starch bloc, and further work on this method of purification is being continued.

A few batches of fermentation were run in a 40-litre stainless steel fermentor with aeration and agitation. These larger batches gave a culture filtrate with twice the enzyme activity compared to the shake flask fermentations. There was however a much larger production of mucilaginous substance, which interferes with purification. The enzymes produced in the larger fermentations have been successfully used to digest vegetable and animal proteins to give peptones. Other uses of the enzyme fraction are under study.

#### (b) Proteases of fungi

The detrimental effect of increasing the concentration of glucose in the culture medium on proteolytic activity, mentioned previously, was confirmed on six strains of A. flavus oryzae. This effect was traced to the effect of glucose on acidity; the pH was reduced to 4.0-4.5, when glucose concentration in the medium was 6%. The enzymic activity at the highest glucose concentration used was reduced to 10% of the activity without

glucose. The study of effect of pH on activity between pH 4 and 9 showed a similar effect, the optimum pH lying between 6.5 and 7.5. The effect of pH on the two activities, viscosity reduction and amino nitrogen release did not show any difference to justify the consideration of these two activities as due to different enzymes.

Large-scale production of enzymes from these strains are under preparation for detailed study of the proteinase and peptidase enzymes.

(c)  $\alpha$ -amino acid acylase of *A.oryzae*

Specificity studies on the  $\alpha$ -amino acid acylase of *A.oryzae* were continued. The susceptibility to hydrolysis of acyl compounds was found to decrease as follows: phenylalanine, methionine, tryptophane, alanine, histidine, aspartic acid. The isolation of the pure enantiomorphs from enzymic hydrolysates of derivatives of DL-amino acids was also carried out.

The acylase from *A.oryzae* was found to be a metal-activated enzyme being inhibited by the metal-chelating agent ethylenediamine tetra-acetic acid (EDTA). The enzyme was completely inactive after treatment with EDTA and dialysis and was reactivated by  $Zn^{++}$  and  $Fe^{++}$  whereas  $Co^{++}$ ,  $Mn^{++}$ ,  $Mg^{++}$ ,  $Cu^{++}$  and  $Fe^{+++}$  were without effect.

(d) Pectic enzymes

Citrus peel extract (containing 2% pectin) was found to be a good substitute for pectin, as also solid bran in place of bran extract, employed in previous medium. The production of the enzyme using the modified medium was about four times that obtained earlier. In aerated and agitated cultures, the amount of air that was found to be optimum was 1.5 litres per minute. The recovery of the enzymes on concentration in vacuo at 30°C was about 95%; the concentrate on precipitation with 2 vols. of alcohol contained 90% of the original activity.



(e) Bacterial amylase

Thirtytwo strains of Bacillus subtilis obtained from N.C.I.M. were examined for  $\alpha$ -amylase (liquefying) activity in surface and submerged cultures. One of them was selected for further experiments towards the development of a medium suitable for large-scale production of the enzyme. In shake cultures a 5% wheat bran extract was found to produce about 3 times the enzyme activity compared to a control containing 2% starch.

(f) Preparation of bacteriological peptones

Using the protease from B.licheniformis peptones for bacteriological use were prepared from sources like casein, egg albumin and defatted peanut powder. These were found comparable to Difco peptone in supporting growth of a variety of micro-organisms.

IV. PROTEIN CHEMISTRY

(a) Analytical behaviour of tryptophan peptides

Investigations on the analytical behaviour of tryptophan in combination have been completed. This work was taken up because methods of tryptophan analysis are usually applied to intact or partially digested proteins and it is essential to know the behaviour of tryptophan peptides with the usual tryptophan reagents.

Several tryptophan peptides and peptide derivatives were synthesised and their colour values determined with the glyoxylic acid reagent. Compared to l-tryptophan, the % of colour given by the peptides were: gly-l-try, 174; chloroacetyl-l-try, 170; carbobenzoxy-gly-l-try, 180; carbobenzyloxyl-ala-l-try, 174; gly-l-try-gly, 79.3; carbobenzoxy-gly-l-try-gly, 91; l-try-gly-gly, 58.6. These results show that the aldehyde reactions which are usually used for colorimetric estimation cannot be used in protein hydrolysates in which the tryptophan is likely to be present as peptides.

The microbiological methods for the estimation of trypto-



phan were also tried on some of these tryptophan compounds. It was found that Lactobacillus arabinosus 17-5, utilises the amino acid in DL-tryptophan to the extent of 40-45%, gly-1-try 85%, 1-try-gly-gly 87%, gly-1-try-gly 40%; the corresponding values for Streptococcus faecalis R were DL-tryptophan 50%, gly-1-gly-tr 40-45%, 1-try-gly-gly and gly-1-try-gly less than 10%. Therefore the microbiological methods also are not applicable to solutions in which tryptophan is present in peptide form; however as DL-tryptophan behaves normally with Streptococcus faecalis R, alkaline hydrolysates of proteins can be used for assays with this micro-organism.

(b) Shark ray elastoidin

Determination of the amino acid composition of shark ray elastoidin was repeated and the values previously obtained confirmed. The amino acid distribution in general follows the pattern characteristic of collagens and justified the inclusion of elastoidin in the collagen group of proteins made on the basis of physical studies. Striking deviations from collagen composition are a high content of tyrosine and a significant amount of cystine; these differences may be of relevance in connection with the peculiar hydrothermal behaviour of elastoidin which distinguishes it from other collagens.

The behaviour of tyrosine and cystine on treatment of elastoidin with hot water, as in the extraction of gelatin from collagen, is being studied.

(c) Preparation of amino acids from cheap raw materials

Further lots of glutamic acid and arginine were prepared on a semi-large scale from groundnut cake hydrolysates.

For the preparation of leucine, histidine and lysine cattle blood from slaughter houses was found to be a richer source. Leucine and histidine were prepared by the classical methods while lysine was prepared by using Amberlite IRC-50 in the sodium form, which selectively adsorbs lysine in the absence

of arginine and histidine. The adsorbed amino acid was eluted with 2 N-HCl and purified from the inorganic salts and acid by adsorption on Dowex-50 (H form). The pure product was finally isolated as the hydrochloride after elution from Dowex-50 by baryta or 5-N sulphuric acid.

With this, the scheme on preparation of amino acids from cheap raw materials has been concluded.

The following amino acids were prepared and supplied as a routine to other institutions, under the Research Chemical Scheme: glutamic acid, arginine, leucine, histidine, cystine and tryptophan.

#### (d) Asparagine from Bengal gram seedlings

Experiments on the large-scale preparation of asparagine from etiolated Bengal gram seeds were undertaken. The method of alcohol dialysis (cf. Damodaran and Chanan Singh) was employed for the isolation of asparagine. Spraying the seedlings with 0.1 M ammonium chloride solution during growth resulted in a higher yield of asparagine.

Two dimensional paper chromatograph of 70% alcohol extract of Bengal gram seedlings grown in diffused light, indicated the presence of the following ninhydrin reacting substances: aspartic acid, glutamic acid, serine,  $\alpha$ -amino adipic acid, glycine, asparagine, threonine, alanine, glutamine, histidine, lysine, arginine, proline,  $\gamma$ -amino-butyric acid,  $\beta$ -alanine, tryptophan, tyrosine, methionine, valine, leucine, isoleucine, phenylalanine.

#### Biosynthesis of nicotine

A clone of isolated tobacco roots was established with a view to study the biosynthesis of nicotine. Various media were tried for the maintenance of the isolated roots in sterile culture. Dawson's medium containing 4% sucrose and White's standard medium minus glycine were found to be satisfactory.

In the latter medium, an inoculum of 20 mm. attained a length of 135 mm, grew 17 laterals and had a fresh wt. of about 34 mg. at the end of 5 weeks growth. Incorporation of glycine at concentrations of 3 mg/l and 5 mg/l in the medium inhibited the growth of roots. Paper chromatographic studies of spent culture solutions revealed that the strain of roots used, synthesise mainly nicotine and some other alkaloid-like material which shows absorption in ultraviolet light.

(e) Polymerisation of tripeptide esters of amino acids

DL-phenylalanyl-glycyl-glycine ethyl ester and L-leucyl-glycyl-glycine ethyl ester were polymerised by heating at 100° for 240 hours and the final products were purified by washing with alcohol. Amino N (Van Slyke) determination indicated about 10 tripeptide units in the final product. Pepsin and trypsin had no apparent action on the polymer ester or the free polypeptide.

Further work on the preparation of different polymers and the study of enzyme action is in progress.

(f) Casein phosphopeptone

Two fractions L<sub>1</sub> and L<sub>2</sub>, from casein phosphopeptone obtained by elution from a Dowex-2 mono-chloroacetate column with 0.01 N monochloroacetic acid and moving to the cathode on continuous paper electrophoresis, using N-acetic acid as electrolyte, contained no phosphorus.

The fraction M eluted with 0.1 N-monochloroacetic acid from the resin and with N-acetic acid in the paper electrophoretic run had a N/P ratio of 7, total N/amino N 7 and contained glutamic acid with free NH<sub>2</sub>-end group. The maximum molecular weight of the fraction determined from its diffusion constant was about 800. Fraction M contained mainly glutamic acid (45% on the N basis) and serine (21%), and smaller proportions of valine (7.5%), threonine (6.2%), aspartic acid (6.1%), isoleucine (5.9%), glycine (3.5%), alanine (3%) and leucine (2%).

The amino acid composition indicated lack of homogeneity although fraction M was electrophoretically homogeneous at pH 2.4 and 6.0.

The three fractions  $R_1$ ,  $R_2$  and  $R_3$  eluted by 0.5 N, N and 5-N monochloroacetic acid respectively from the resin and moving towards the anode in the order  $R_1$ ,  $R_2$ ,  $R_3$  in the electrophoretic runs with N-acetic acid, contained markedly higher proportions of serine, the serine and glutamic acid N contents being 27 and 36% respectively in  $R_1$ , 26 and 38% in  $R_2$  and 45 and 23% in  $R_3$ . Fractions  $R_1$  and  $R_2$  contained 9-10% isoleucine, 5-6% each of aspartic acid and threonine and smaller proportions of glycine, alanine, valine, isoleucine and leucine. Fraction  $R_3$  contained glycine 8%, alanine 6.9%, valine 5.6%, isoleucine 15.4% and leucine 4.1%, but no aspartic acid or threonine. The amino acid composition of the three fractions again showed lack of homogeneity. All the P containing peptide fractions obtained from casein phosphopeptone by paper electrophoresis as well as by gradient elution from Dowex-2 monochloroacetate columns are probably each a group of closely related peptides.

## V. PROTEIN METABOLISM

### (a) Transfusion gelatin

The survival rate of dogs bled to 50% of initial blood volume when given no transfusion was studied. 30% of the animals were found to survive for four hours without transfusion; a much higher rate of survival should, therefore, be considered necessary, to prove the efficiency of a plasma substitute.

The effect of the NCL modified gelatin, Knox P-20 gelatin, Intradex, Dextraven, plasma and saline on erythrocyte sedimentation rate (ESR) was studied in vitro. It was found that modified gelatin solution (8%) when mixed with human blood in the ratio of 1:9 affected the ESR only slightly. Higher proportions showed a marked increase in the effect. Modified gelatin had the same effect on ESR as human plasma while

Dextraven and Intradex had a much more pronounced effect.  
Normal saline was without effect.

The wt. average molecular weight of the following transfusion gelatin preparations were determined by the light scattering method in collaboration with the Physical Chemistry Division:

- i) Knox P-20 gelatin
- ii) gelatin before treatment with trypsin
- iii) gelatin treated with trypsin for 10 minutes (modified gelatin)
- iv) gelatin treated with trypsin for 15 minutes.

The preliminary results were as follows:

Gelatin sample	Knox-P-20	Gelatin before treatment with trypsin	Gelatin treated with trypsin	
			for 10 mts.	for 15 mts.
Mol.Wt.	46,000	115,000	56,000	30,000

(b) Proteins and amino acids in blood formation

Feeding experiments showed that hydrolysed zein even when supplemented with tryptophan and lysine does not promote optimum growth and haematopoiesis in albino rats and suggested the need to investigate the possible presence of enzyme resistant peptides in the zein molecule. For <sup>this</sup> purpose sufficient quantity of zein was hydrolysed by 6 N-HCl and the applicability of ion-exchange resins for removing the HCl from the hydrolysate was investigated. Among the resins tried IRA-400 in the acetate form was found to be the most effective, the amino acid mixture after the resin treatment being found to be almost free from HCl and acetic acid. In this procedure the loss of N in the preparation of amino acids amounted only to 5%. Feeding experiments on the relative efficiency of zein and zein hydrolysate in maintenance of growth and Hb formation is now being carried out.

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## VI. MICROBIOLOGICAL PRODUCTION OF SULPHUR

### Sulphate reduction by *Desulphovibrio desulphuricans*

(a) Hydrogenase, which participates in the reduction of sulphate by hydrogen, was obtained from *Desulphovibrio desulphuricans* in a state of high purity. Its properties and kinetics were studied. After treatment with acetone in acid solution the enzyme was shown to be activated by the addition of ferrous or ferric salts.

(b) The microbiological production of sulphur from inorganic sulphate by *D. desulfuricans* has been studied. This organism which has hitherto been shown to reduce only inorganic sulphur compounds to  $H_2S$ , has now been shown to reduce organic thiosulphates to hydrogen sulphide and the corresponding thio derivative L-cysteine-S-sulfonate was reduced quantitatively to cysteine and  $H_2S$  with the absorption of four equivalents of hydrogen. Ethyl thiosulphate was similarly reduced to ethyl mercaptan and  $H_2S$ . Aged bacterial cells reduced inorganic sulphate very slowly and showed a lag period before maximum activity was observed. The addition of organic thiosulphates abolished the lag period and increased the rate of sulphate reduction by 200 to 300 per cent. The formation and role of organic thiosulphate in sulphate reduction is being studied.

## VII. PHOSPHORUS METABOLISM IN MOULDS

Metaphosphate has been shown to be present in the mycelium and spores of *Aspergillus niger*. The formation of soluble and insoluble metaphosphate in surface and submerged cultures of NRRL-599 was studied. In the initially formed mycelium the concentration of the insoluble form was five times greater than that of the soluble form. The soluble compound increased to a maximum after 1-2 weeks and then decreased, but with the onset of autolysis it showed a rapid increase. Trace amounts of zinc markedly increased the concentration of soluble

metaphosphate. The insoluble compound in surface cultures decreased from the initially high values during fermentation, whereas it maintained a uniformly high value in submerged mycelia.

The major portion of the labile phosphate of the spores has been shown to consist of metaphosphate, which was isolated as the barium salt and identified by rate of hydrolysis, chromatography and the meta-chromatic assay. Its molecular weight was approximately 300. A hexametaphosphate was similarly isolated from the mycelium of A.niger as the Ba salt. A study of 4 different cultures of A.niger indicated that the metaphosphate metabolism was probably closely related to that of ribonucleic acid.

#### VIII. BIOSYNTHESIS OF LABELLED COMPOUNDS

##### (a) Preparation of glucose and fructose by photosynthesis

Photosynthesis was carried out with tobacco leaves placed in a perspex chamber in which an atmosphere of  $C^{14}O_2$  was maintained. After exposure to light the leaves were killed in boiling alcohol and worked up for the isolation of the carbohydrates. The leaf residue contained starch while the alcoholic extract contained glucose, fructose and sucrose. The starch was not isolated as such, but was hydrolysed to glucose by enzymic hydrolysis by salivary amylase followed by a low concentration of mineral acid. The hydrolysate was de-ionised with cation and anionic resins (Amberlite); on concentration and treatment with ethyl alcohol it yielded crystalline glucose.

From the alcoholic solution, separation of glucose and fructose with simultaneous hydrolysis of sucrose was achieved by catalysis with an ion-exchange resin (Amberlite IR-120) in  $H^+$  phase in the presence of acetone. Fructose was converted to di-isopropylidene derivative and went into solution while glucose remained unacted on and separated out. Glucose was washed out of the resin with water and crystallised by fractiona-



tion with alcohol. Fructose was obtained by decomposing the di-acetone-fructose by 0.03 N mineral acid which was later removed by an anion-exchange resin. Fructose was crystallised out by using a solvent system of ethanol and acetone.

(b) A new source of desoxyribose

The sugar detected in Buddlia lindeni leaves by paper chromatography responded to the desoxyribose reaction. A preliminary fractionation involving extraction with various solvents such as water, alcohol, butanol and ethylacetate and chromatography over cellulose, hyflosupercell carbon and ion-exchange resin resulted in about 10 to 20 fold concentration of the sugar. Further studies in purification of the sugar are in progress.

IX. NATIONAL COLLECTION OF INDUSTRIAL MICRO-ORGANISMS

The routine subculturing and maintenance of the organisms in the collection were carried out.

Cultures were regularly supplied to the staff of the Biochemistry Division for projects on the production of amylase, pectinase, sorbose, protease and for microbiological assay.

During the year 175 cultures were distributed to about 80 institutions including those in U.K., U.S.A., Canada and Australia.

51 new cultures have been added from foreign collections.

At the request of the Dyeing and Printing Experimental Laboratory, Poona, (Cottage Industries Dept., Govt. of Bombay), the vat liquor <sup>/ samples from</sup> ~~is~~ some villages where indigo was converted to the leucoform by fermentation <sup>were</sup> ~~was~~ examined. 28 bacteria were isolated from the indigo vat liquors; these were prepared in pure cultures, and a preliminary study was made of their properties, in particular, reduction of indigo.

30 bacteria have been isolated and purified from garden soil by plating on a cholesterol medium. Six of these cultures grow very well on cholesterol media and are under study.

35 membranes (6" x 1/2") produced by Acetobacterxylinum were supplied to the Plastics & Polymers Division, N.C.L. and 6 membranes were supplied to the Indian Institute of Technology, Kharagpur.

The morphology of yeast and Aspergillus niger grown under stationery and shake conditions were studied by electron microscopy and phase contrast microscopy, in collaboration with the Physical Chemistry Division, N.C.L. These studies, which are in the preliminary stages, have shown interesting differences in morphology, according to the conditions of cultivation.

In collaboration with the Radioactive Tracer Laboratory, the effect of  $\beta$ -rays from Yttrium-90 on a strain of Saccharomyces cerevisiae was studied. A fast growing sector gave a mutant, which differed from the parent strain in its inability to ferment galactose. The heritable character of this change is under study.

#### CHEMICAL ENGINEERING DIVISION

##### I. CARBON BLACK PILOT PLANT

The second and larger pilot plant has been operated during the year and better carbon blacks have been produced than were obtained in the first plant. A number of oils such as fuel oil, heavy and light duty diesel oils, recycle oil, etc., have been used. The carbon blacks produced are being tested in respect of their physical characteristics and performance in rubber formulations.

##### II. PHYSICO-CHEMICAL CHARACTERISTICS OF HIGH-CALCIUM INDIAN LIMESTONES

50 samples of limestone drawn from high-grade deposits throughout India have been evaluated in terms of their physico-chemical properties for specific applications in the chemical industry. The same has been done in respect of the quicklines

and hydrated lines obtained from these limestones.

This work will be of interest and value to all sections of the chemical industry concerned with the production or consumption of limestone and lime. A monograph dealing with this work is under preparation.

Collection of limestone samples from East Punjab, Uttar Pradesh, and Assam, has been initiated through the Geological Survey of India. These States were not included in the first study which has been completed and the new samples will be included in a second monograph.

### III. BLEACHING POWDER

Investigations on the effect of temperature, humidity and impurities contained in lime on the stability of bleaching powder have been completed. The suitability of various Indian lines for the production of stable bleaching powder has been assessed. The results are being published in India and abroad.

This work should be useful to the Indian bleaching powder industry in connection with the production of stable bleaching powder.

### IV. NICOTINE SULPHATE FROM TOBACCO WASTE

The new process developed at this Laboratory for the production of nicotine sulphate from tobacco waste has been leased for commercial exploitation to M/s Tobacco By-products Ltd. Guntur, who have a factory under erection at Guntur. Equipment design and factory lay-out have been done for the firm by the Laboratory.

### V. POLYVINYL CHLORIDE FROM ALCOHOL

The pressure vessels for the condensation and polymerization of vinyl chloride were made as nearly leakproof as possible and were fitted up on the bench-scale assembly. However, as the actual condensation and polymerization experiments presented certain difficulties and as regular routine runs on this scale would be expensive, work was initiated on a smaller

scale using a stainless steel tube provided with a screw cap fabricated to withstand about 200 psig as the polymerization vessel. Small batches of polyvinyl chloride have been prepared in this apparatus. Molecular weights of the experimental batches of polyvinyl chloride are being determined. Further work is in progress to establish the optimum conditions of polymerization.

Delivery of the larger pilot plant is awaited from the fabricators.

#### VI. MASS TRANSFER IN A PULSED EXTRACTION COLUMN

Equipment has been designed and assembled to study the influence of sinusoidal pulsations on mass transfer in a counter-current liquid-liquid extraction column. The system being used initially is benzene-acetic acid-water. Preliminary experiments have shown that the value of HTU is reduced by pulsing the column. The variables being studied are: pulse frequency, pulse amplitude and liquid flow rates.

#### VII. PULSED FLOW HEAT TRANSFER

The object of this investigation is to study the influence of pulsations on heat transfer coefficients in heat exchangers. The apparatus used employs a single tube heat exchanger with steam condensing on the outside or water flowing inside the tube. Pulses are provided by a reciprocating pump. Runs made in the Reynold's number range of 6000 - 80,000 have not shown any increase in the value of steady-flow heat transfer coefficients as a result of pulsation. Runs are being made at lower Reynold's numbers. It is proposed to use glycerine in place of water in a subsequent series of runs and also to vary the pulse frequency.

#### VIII. PREFERENTIAL CHLORINATION OF IRON FROM ILMENITE IN A FLUIDIZED BED

It has been possible to remove almost 95% of the iron in ilmenite without appreciable loss of titanium. The fluidized bed chlorination process offers distinct advantages over a

fixed bed for the reaction.

A study of the kinetics of the preferential chlorination of iron is in progress with a view to developing a rate equation for the reaction.

### INORGANIC DIVISION

#### I. FERTILISERS AND RELATED PRODUCTS

With a view to conserving sulphuric acid, a mixed nitrogen-phosphorus fertilizer has been prepared from rock phosphate, ammonium sulphate and hydrochloric acid. Using the same acid, dicalcium phosphate has been prepared, on a pilot-plant scale from Kossier rock phosphate or Trichinopoly phosphatic nodules.

Valuable phosphatic materials such as ammonium phosphate fertiliser and sodium tripolyphosphate detergent, have been obtained by simple processes from trisodium phosphate, a by-product from the Indian Rare Earth Factory. Powder diffraction patterns of tripolyphosphates (prepared at both high and low temperatures) showed that they are similar to the corresponding products obtained from American manufacturers. Ammonium phosphates have been prepared in different grades which are comparable with the imported ones and range from weakly acidic to weakly basic products.

Two major products of the Indian marine salt industry, impure gypsum and a "bittern", (containing principally magnesium sulphate, magnesium chloride and small amount of sodium and potassium chlorides) run practically to waste. A process has been worked out using these magnesium salts to fix ammonia to produce a mixed fertilizer with an available nitrogen content of 22% and potash 4%. Light basic magnesium carbonate and light magnesia, useful for making refractories, are obtained as by-products.

## II. ACTIVE MANGANESE DIOXIDE FOR DRY BATTERIES

Indian pyrolusite is unsuitable for the manufacture of dry batteries. Manganese dioxide of a special crystalline structure is imported in the form of a natural mineral or as synthetic material for this purpose.

A manganese dioxide of appropriate crystalline structure has been obtained by precipitating the hydrated dioxide from an impure manganese sulphate solution with chlorine. The product has been made into dry cells which were tested for their discharge current and voltage characteristics. The new cells were found to give as good a performance as the best dry cells on the market.

The process appears to be quite suitable for low grade ores which have little market value. Details of the process are embodied in C.S.I.R. patent No. 54395.

## III. SYNTHETIC CRYOLITE

With a view to replace imported cryolite by synthetic cryolite in the aluminium industry, cryolite from sodium fluoride has been successfully prepared. Subsequently, a new and rapid process was evolved for the preparation of sodium fluoride by heating Indian fluorspar with soda ash in presence of some oxide catalysts.

## IV. TITANIUM PRODUCTS

Indigenous sources of titanium, viz., ilmenite; rutile and bauxite sludge were chlorinated to isolate pure titanium tetrachloride, which was hydrolysed under suitable conditions to give pure white rutile titania.

A sulphuric acid process for making anatase titania from bauxite sludge has been worked out in which the sludge is first upgraded by leaching out a part of the iron and aluminium oxides with hydrochloric acid and subsequently removing most of alumina as potash alum which forms a useful by-product of the process.

Titanium tetrachloride was reacted with fusel oil to

give esters which were used successfully in place of butyl titanate. The incorporation of titanium or silicon into cashewnut shell liquid-formaldehyde varnish gave rise to a new product which possessed properties of high insulation and high plasticity. The product is likely to find application in manufacture of radio components.

#### V. STUDIES IN THE CHEMISTRY OF RARE ELEMENTS

These include (a) development of suitable chemical methods for extraction of rare elements from Indian raw materials, (b) purification of a low-grade material, or, separation of individual components of a mixture in a high grade of purity, and (c) evolution of rapid methods of their estimation when present in minute quantities.

Germanium was extracted from flue dust as a complex oxalate. Its recovery by electrolysis as a co-deposit with nickel was a new observation, and <sup>was</sup> the first successful attempt at its quantitative recovery by electrolysis of very dilute solutions.

Commercial selenium contains impurities which vitally impair its use in rectifiers and photo-electric cells. The problem was undertaken on request from a firm which supplied the commercial material. A new process has been developed for obtaining a product free from the associated impurities.

Zirconia has been obtained from Indian zircon by a simple chemical process. Sodium silicate was obtained as a by-product. Zirconia, thus obtained contains 2-3% hafnia, whose removal is important in connection with atomic energy work. A new ion-exchange method has been developed which isolates 90% of the zirconia and some hafnia both in spectroscopically pure forms.

The technique of high temperature chlorination was used successfully to prepare niobium-tantalum chloride and phosphate-free rare earth chlorides from Indian monazite. Mixed chlorides of the rare earths, now obtained as a by-product in the Indian Rare Earths Factory, are being chemically treated for the separa-



tion of individual light rare earths in a state of purity.

## VI. NEW ANALYTICAL METHODS AND TECHNIQUES

The polarograph, spectrograph and the flame photometer have been used for service work associated with research projects. New analytical methods developed during the year include a polarographic method for niobium, a spectrographic method for hafnium in zirconium, a microgravimetric method for germanium, spectrophotometric method for tantalum and for cerium, and a volumetric method for total and active acids in a sulphate solution of iron, aluminium and titanium.

## ORGANIC CHEMISTRY DIVISION

### I. SYNTHESIS OF XANTHONES

The new and simple method of synthesis of xanthenes evolved in this Laboratory and reported last year, has been employed for the synthesis of a large number of hydroxy and partially methylated hydroxy xanthenes including some naturally occurring xanthenes, like gentisein and lichexanthone and derivatives of naturally occurring xanthenes like swertinin dimethyl ether and swerchirin dimethyl ether. Thus the general applicability of the new method has been firmly established. Further, the synthesis of swerchirin dimethyl ether and swertinin dimethyl ether conclusively establishes the structure of the naturally occurring xanthenes, swerchirin and swertinin as methyl ethers of 1:3:5:8-tetrahydroxy xanthone and 1:3:7:8-tetrahydroxy xanthone respectively.

### II. PHOSPHORUS OXYCHLORIDE-ZINC CHLORIDE MIXTURE AS A NEW CONDENSING AGENT IN ORGANIC SYNTHESIS

A mixture of phosphorus oxychloride and anhydrous zinc chloride has been established to be a new condensing agent of wide applicability in organic synthesis. Most of the reactions take place at the room temperature often giving yields as good or even better than those obtained by using the conventional methods such as Friedel - Crafts, Fries and Hoesch reactions,

involving more than one step. The new condensing agent has been successfully employed for the synthesis of a large number of hydroxy, alkoxy or aryloxy aryl alkyl ketones, deoxybenzoins, benzophenones, chalkones and phthaleins. Some of the products prepared by this simpler method, such as hexyl resorcinol (intermediate for the preparation of the important antiseptic hexyl resorcinol), p-methoxy propiophenone and deoxyanisoin (intermediates for the preparation of important synthetic oestrogens hexesterol and stilbesterol) are of technical importance.

### III. COUMARINS

4-Acetomethyl-5-methyl-7-methoxycoumarin, m.p. 156-57° has been finally synthesised from 5-methyl-7-methoxycoumarin-4-acetic acid by conversion of the latter, first to acyl chloride and then to the corresponding diazoketone which was finally reduced to the required acetomethylcoumarin.

The synthetic coumarin does not agree with the Kostanocki acetylation product of oracetophenone monomethyl ether, which would, therefore, most probably have the alternative structure of 3-acetyl-4:5-dimethyl-7-methoxycoumarin.

### 4. SYNTHESIS OF FLAVAN-DIOLS

All the four possible racemates of flavan 3:4-diol were synthesised by different methods and the respective configurations were assigned to them on the basis of experimental data and conformational analysis. The stereochemistry of the intermediate dihydroflavonol and the 3-bromoflavan-4-ol was also studied and conformations assigned to them.

### V. SYNTHESIS OF GEIJERIN

Geijerin, a naturally occurring coumarin to which the structure of 7-methoxy-6-isovelerylcoumarin had been assigned has now been synthesised in this Laboratory and found to be identical with the natural product. The present synthesis confirms the structure assigned to it.

## VI. SYNTHESIS OF VITAMIN A

Vitamin A is commercially synthesised by condensing a  $C_{14}$ -aldehyde, which is obtained from citral, with a  $C_6$ -acetylenic compound.

Pseudo-ionone, obtained by condensing citral (in Malabar lemongrass oil) with acetone has been converted to  $\beta$ -ionone in 60% yield by a method developed in this Laboratory. The  $C_{14}$ -aldehyde has been obtained from the latter in very good yields.

Work on the preparation of the  $C_6$ -acetylenic intermediate by condensing vinyl methyl ketone with sodium acetylide is in progress.

## VII. GLORIOSA SUPERBA

Gloriosine has been found to have the structure of N-formyl-isodesacetyl colchicine.

## VIII. ACONITE ALKALOID

Aconitine, on oxidation with aluminium tertiary butoxide or chromic acid yielded aconitone which on heating at the melting point loses a molecule of methyl alcohol and changes to aconitoline.

Pyrolysis of aconitine at  $250-60^{\circ}$  under reduced pressure gave acetic acid, a colourless crystalline product, m.p.  $124^{\circ}$  and a resinous product, m.p.  $148-50^{\circ}$ . These products have been partially characterised.

## IX. CHEMICAL INVESTIGATION OF MUNDULEA SUBEROSA

A new crystalline product, munetone, has been isolated from the root bark of the indigenous fish-poison plant *Mundulea suberosa*. From the results so far obtained, munetone appears to be a new isoflavone derivative. This is of interest as the known plant insecticides do not contain the isoflavone skeleton.

## X. PRISTIMERIN

In continuation of the work on the constitution of pristimerin, experiments on the oxidation, reduction and hydro-

lysis of pristimerin and some of its derivatives have been carried out.

#### XI. SUGARCANE WAX

Analysis of the different fractions of methyl esters of sugarcane wax acids was completed.

#### XII. MANUFACTURE AND EXPERIMENTAL APPLICATION OF HORMONE TYPE OF HERBICIDES AND WEEDICIDES FOR WEED CONTROL

Large quantity samples of T.C.A. have been prepared and sent to Indian Agricultural Research Institute, New Delhi, for field experiments.

Five different thioureas, two thiocarbamates, and a substituted phenoxy acetic acid have been prepared and sent to the College of Agriculture, Poona, for testing their herbicidal properties.

#### XIII. BITTER CONSTITUENTS OF NIM OIL

The eight oxygenic functions of the molecule of nimbin, the principal crystalline bitter constituent of nim, were accounted for by the presence of an aldehydic, a lactonic, a methoxy, an acetoxy and an ester grouping in the molecule. The data so far obtained suggest that nimbin belongs to the group of steroidal cardiac-active principle.

Sufficiently large quantities of sodium nimbidinate have been prepared and supplied to the C.S.I.R. Pharmacological Unit in the G.S. Medical College, Bombay, for studies in the diuretic properties of the compound.

#### XIV. PILOT-PLANT WORK ON NIM OIL

Several runs have been made in the De Laval Unit for the partial refining of nim oil after extraction with alcohol.

Samples of the refined oil have been sent to the Village Industries Laboratory, Govt. of Bombay, for assessing their suitability for making good quality soaps.

#### XV. CALOPHYLLUM INOPHYLLUM OIL

From the data so far obtained, inophyllic acid appears to have the structure of a highly unsaturated long chain

acid containing a keto group and a benzene ring.

Action of ethyl inophyllate on cases of leprosy is being studied in collaboration with the local Medical College and the Corporation.

#### XVI. STERCULIA FOETIDE OIL - STRUCTURE OF STERCULIC ACID

The new structure proposed for sterculic acid, reported last year, has been supported by the evidence obtained from a study of its ozonisation, hydroxylation and oxidative degradation products.

#### XVII. PAINTS AND VARNISHES

##### (a) Alkyd resins from kamala seed oil

Alkyd resins have been prepared from total kamala seed oil extractable with benzene and from kamalolenic acid. The properties of the films of these resins were found to be almost similar to those prepared from tung oil and also some commercial alkyd resins.

##### (b) Heat treatment of kamala seed oil

Kamala seed oil extractable with benzene and its fractions from hexane and petroleum ether (40-60°C) were submitted to heat at 100°C, 150°C and 200°C both in ordinary atmosphere and in nitrogen. The periods of gelation and other changes in physical and chemical properties that various oil samples underwent as a result of the heat treatment have been recorded and compared with the similar data obtained with tung oil.

##### (c) Anticorrosive paints

Varnish bases have been prepared from linseed stand oil and rosin, maleated rosin, CNSL-rosin condensates, CNSL-dry oil fatty acid condensates and various properties of the film of these coating compositions have been determined. A paint prepared from the linseed oil-rosin varnish base has been sent to the Indian Naval Dockyard Laboratory for raft-test. Films prepared from maleated rosin have been found satisfactory as regards water resistance. A paint from this varnish base is

under preparation for sending for raft-test at the above Laboratory.

XVIII. PRODUCTION OF 12 - AND 18-HYDROXYSTEARIC ACIDS AND SOME COMPOUNDS FROM THEM

12- and 18- hydroxy-stearic acids have been prepared by hydrogenation of tri-ricinolein and kamolonic acid isolated from castor and kamala seed oils using commercial nickel catalyst. Their lactonisation and preparation of hexadecancthylenic-1:16-dicarboxylic acid from 18-hydroxystearic acid have been carried out.

XIX. MOLECULAR CONSTITUTION OF KAMALA SEED OIL

Total kamala seed oil extracted with ethyl ether has been fractionated in a number of fractions by chromatography, differential solubilities in various solvents and by low temperature crystallisation procedure. The work on the determination of chemical and physical characteristics and the fatty acid analysis of various fractions is in progress.

XX. NICKEL CATALYST FOR THE HYDROGENATION OF VEGETABLE OILS

Samples of nickel catalyst from nickel formate have been prepared at various temperatures. The most effective catalyst has been selected and favourable conditions as regards to the amount of catalyst, pressure and temperature of hydrogenation have been established.

XXI. IDENTIFICATION OF DIFFERENT VEGETABLE OILS

(a) Hexabromide value for estimation of linolenic acid

A procedure for the estimation of linolenic acid in fatty acid mixture by the determination of hexabromostearic acid has been developed which was found to give results identical to those obtained by ultraviolet spectroscopy technique.

(b) Tetrabromide value for the estimation of linoleic acid

A method has been developed for the determination of linoleic acid in fatty acid mixtures by the estimation of tetrabromides formed. The results obtained were found to be almost

similar to those obtained by ultraviolet spectroscopy technique.

#### XXII. STABILIZATION OF EDIBLE FATS BY SPECIES

Hydroxychavicol, isolated from betel leaves, exhibits a strong antioxidant effect when used with groundnut oil and lard and is comparable to some of the well known antioxidants used for stabilising edible fats. The antioxidant effect of red chillies seems to be due to the synergistic action of ascorbic acid in combination with the natural antioxidants present in the oils.

#### XXIII. N-BROMOSUCCINIMIDE IN THE PRODUCTION OF CONJUGATION IN FATTY ACIDS

Bromine of N-Bromosuccinimide attaches itself with the carbon atom adjacent to the double bond in monoethenoid fatty acids. The brominated product on heating under standard conditions evolve hydrobromic acid and a conjugated double bond is created.

#### XXIV. CYCLIC PERFUMERY MATERIALS

Two routes for the preparation of civetone dicarboxylic acid have been established and three patents on the subject have been filed. Experiments on the large scale preparation of the acid are in progress.

A process for the preparation of musk acid has been established.

#### XXV. INDIAN SPEARMINT OIL

Mint-glyoxal, the unusual glyoxal derivative isolated from the oil has been cyclised to thymol, which established the structure assigned to it earlier.

#### XXVI. DIHYDROJASMONE

A new method for the preparation of dihydrojasnone has been investigated.

#### XXVII. MISCELLANEOUS ESSENTIAL OIL COMPONENTS

Several new sesquiterpenic components have been isolated from various Indian essential oils and their structures



established. One of these appears to be the first naturally occurring saturated humulene derivative.

#### XXVIII. INFRA-RED SPECTROSCOPY OF SOME ESSENTIAL OILS

A new method for the evaluation of sandalwood oil through infra-red spectroscopy has been investigated and is likely to be of considerable commercial utility.

#### XXIX. A NEW ORGANIC REAGENT FOR QUANTITATIVE ESTIMATION OF COPPER AND PALLADIUM

3-hydroxy-1:3-diphenyltriazine, a compound recently synthesised in this Laboratory has been found to be a highly selective reagent for the estimation of copper and palladium. The reagent forms directly weighable complexes with copper and palladium. Sulphonic acid derivative of the compound has been found to be a suitable colorimetric reagent for palladium and molybdenum.

#### XXX. MICRO-ANALYSIS

##### (a) Micro-analytical research

A rapid and continuous method for the estimation of nitrogen has been developed and successfully employed in the analysis of even difficultly combustible substances which normally leave chars.

##### (b) Routine analysis

One hundred and forty-seven analyses were carried out for universities and other outside laboratories and eight hundred and nine analyses were carried out for this Laboratory.

### PHYSICAL CHEMISTRY DIVISION

#### I. ELECTRON AND OPTICAL MICROSCOPY

Studies on evaporated zinc and cadmium films on various substrates revealed that the texture of films depended on the nature of the substrate and could be modified by contaminants such as grease on the substrate surface.

an electron microscopic examination of anodically treated thin aluminium films (prepared by vacuum condensation) showed the films to be structureless if the anodization voltage was slowly raised from zero. On the other hand, the films appeared to be crinkled if they were given a sudden "shock" of about 40V.

The nature and mechanism of epitaxial crystal growth has been studied by growing crystals of ammonium iodide, sodium nitrate and methylene blue from solution on cleavage faces of mica and calcite. The size of the initial nucleus which determined the nature of epitaxy is extremely small and once the nucleus is formed the substrate has no influence on further growth.

A technique has been developed to obtain good preshadowed replicas of surfaces of crystals of long chain fatty acids.

*Saccharomyces Cerevisiae* (Baker's yeast strain) stained with Lugol's iodine and toluidine blue were photomicrographed under aerobic and anaerobic conditions, at various stages of growth. The unstained cultures were also observed under phase contrast. The yeast cells showed maximum dye-adsorption between 4½ and 6 hours after inoculation. Electron micrographs of this sections of yeasts in the shake cultures showed distinct, compact nuclear vacuoles, while those of rest cultures exhibited only single large diffuse vacuoles.

Micro-sections of *Aspergillus niger* spores showed the presence of a heavy core surrounded by a cell-wall having spike-like protrusions.

## II. SURFACE STRUCTURE STUDIES BY ELECTRON DIFFRACTION

### (a) Solid-gas reactions

A study of the progressive action of bromine and iodine vapours at room temperature on (111), (110) and (100) faces of copper as well as on polycrystalline copper has shown that the halides formed grow epitaxially on the Cu faces, inspite of large differences between the lattice parameters of the substrate and the halides. The deposits grew in parallel orientation on

(111) face, while on the (110) and (100) faces, (100) orientation was observed. In the case of the (100) face, the axes of the halide crystals were turned through  $45^\circ$  with respect to the axes of the substrate. Often the growth of halides was accompanied by twinning on 111 planes. With increase in film thickness the layers became random and finally one-degree orientated, the final orientation being determined solely by the mode of reaction.

Oxidation of copper under varying conditions of temperature, pressure and time of reaction showed that the initial oxide layers always consisted of epitaxially grown  $\text{Cu}_2\text{O}$ . At atmospheric pressure, parallel orientation on a (110) face, and mixed (100) and (111) orientation on (100) and (111) faces were observed, often accompanied by twinning on  $\{111\}$  planes of  $\text{Cu}_2\text{O}$ . At temperatures higher than  $200^\circ\text{C}$  two degree  $\text{CuO}$  grew on the epitaxially grown  $\text{Cu}_2\text{O}$ . With increase in film thickness the oxide layers became random and finally one degree orientated.

At lower pressures (0.05 mm Hg)  $\text{Cu}_2\text{O}$  generally grew in parallel orientation finally taking up one degree orientation on prolonged heating. No  $\text{CuO}$  was formed even at  $350^\circ\text{C}$  presumably due to the decomposition of  $\text{CuO}$  to  $\text{Cu}_2\text{O}$  in vacuum. This view has been verified by the fact that under the same conditions  $\text{CuO}$  in thin film even in the absence of metal was found to decompose to  $\text{Cu}_2\text{O}$ , and also one-degree (021)  $\text{CuO}$  changed to (100)  $\text{Cu}_2\text{O}$  in half an hour.

The oxide layers formed as above were reduced in molecular hydrogen and the nature and orientation of the reduced surfaces examined.

Based on the above investigations, a mechanism of oxidation of copper has been deduced.

#### (b) Crystal-growth in cathodic processes

A study of the growth of nickel deposits on various faces of copper under different bath conditions, has shown

that the deposits grow with parallel orientation, sometimes accompanied by twinning on  $\{111\}$  planes of Ni. Under certain bath conditions development of twinned structure was found to be facilitated. The development of (211) orientation was shown to be due to double twinning on the initial (100) orientation. In chloride and sulphate-chloride baths, (210) type of orientation was favoured at low temperatures, which gradually changed to (100) or (1010) and (211) at slightly higher temperatures. Further rise in temperature ( $>50^{\circ}$ ) led to (110) orientation. This sequence of changes was not affected by pH in the range 1-6, although the temperature range favouring a particular orientation may vary with pH.

A study of the effects of certain addition agents in a nickel bath showed that, at and above the incipient precipitation pH of the corresponding hydroxides or isoelectric point of the addition agent, the orientation of electro-deposited Ni changed from lateral to outgrowth type. This has been ascribed to the formation of a semi-permeable membrane near the cathode region, which controlled the supply of the metal ions to be deposited.

Metal deposited from complex baths showed mostly outgrowth type of orientation, due to the low metal ion concentration. Deposits of copper from glycine bath showed an asymmetric orientated pattern not hitherto observed. The cause of this phenomenon is under investigation. The brightening action of thio-urea on silver electrodeposited from argentocyanide baths has been shown to be due to some oxidation products of thiourea.

#### (c) Crystal growth in vapour-phase deposition

Zinc and cadmium were deposited from vapour phase on a glass plate and on a rocksalt cleavage face. The deposits generally developed one-degree orientation, but on the NaCl (100) face, zinc grew in a two-degree orientation also.

### III. X-RAY DIFFRACTION

The decomposition of manganese carbonate in the temperature range  $150^{\circ} - 1100^{\circ}\text{C}$  has been studied and the oxides formed at various temperatures identified. Influence of non-stoichiometric compositions on the lattice parameters of the oxides has been investigated.

A study of the phase transitions occurring in anhydrous sodium sulphate when heated to various temperatures upto its melting point at atmospheric pressure and in vacuum, has shown that the transition temperatures were different in the two cases.

Identification analysis of a large number of samples received from various divisions of this Laboratory and from the outside organisations have been carried out.

### IV. SOLID-SOLID REACTIONS

Several spinels and spinel-like compounds have been prepared by solid-solid reactions, and analysed for detailed structure determination, particularly to correlate their electrical and magnetic properties with the distribution of cations in the lattice.

Following the generalised quantum rate theory, expressions for the reaction kinetics of spinelization reactions have been derived. The rate of reaction has been found to be dependent upon diffusion coefficients, concentrations at interfaces, transport numbers, and valencies of the diffusing ions.

The formation and epitaxial growth of nickel-ferrite on the various faces of haematite single crystals have been investigated by X-ray electron diffraction. The transformation of

$\alpha\text{-Fe}_2\text{O}_3$  to  $\gamma\text{-Fe}_2\text{O}_3$  was found to be a necessary prerequisite to the spinelization reaction. The transformation of

$\alpha\text{-Fe}_2\text{O}_3$  to  $\gamma\text{-Fe}_2\text{O}_3$  seems to occur through a new intermediate phase, designated  $\beta\text{-Fe}_2\text{O}_3$ , in which some of the cations take up tetrahedral sites in the hexagonal framework of the oxygen ions. It is considered possible that the parasitic ferromagnetism of

haematite may be due to the presence of traces of  $\beta$ -Fe<sub>2</sub>O<sub>3</sub> in haematite.

The existence of a super-structure in  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and a new super-structure in nickel-oxide have been identified.

Cadmium and zinc manganites have been prepared by heating the respective oxides at high temperatures. They have been found to form tetragonal unit cells and their detailed structures have been worked out by X-ray. Similar investigations on nickel, copper, iron and cobalt manganites are in progress.

Solid-state reactions between Zr & Te, Ni & Te, Ni & Se and BaO & TiO<sub>2</sub> have been investigated by the Atomic Energy Establishment in collaboration with this Laboratory. The formation of compounds such as ZrTe<sub>2</sub>, Ni<sub>3</sub>Se<sub>2</sub> and Ni<sub>3</sub>Te<sub>2</sub> has been identified and their detailed structures have been worked out by X-ray.

When NaCl and KCl crystals, containing Rb<sup>86</sup> as impurity in their matrices, are heated, the impurity ions preferentially escape from the crystals. It is assumed that under the conditions, the larger Rb ions are subject to higher overlap forces, and migrate to the surface and eventually escape due to greater inelastic scattering with phonons.

#### V. INFRA-RED ABSORPTION STUDIES

Changes in the structure of natural rubber during cyclization at various temperatures have been studied. It has been found that cyclization reaction became pronounced at 80°C and that cyclized rubber contained cyclohexene-type rings. Effect of nuclear radiation on natural rubber in various solvents is being investigated.

A method has been standardized for the estimation of sterculic acid in kernel oil. For the estimation of iso-oleic acid in hydrogenated fats, the modified Twitchell lead salt - alcohol method of Cock et al was found to be comparable in accuracy with the infrared absorption method. Studies on the heat polymerization of karlolenic acid and sterculic acid are

in progress.

A method for the detection of adulteration in sandalwood oil by infra-red absorption spectral analysis has been developed. Analyses of chaulmoogric and hydnocarpic acids, staphisine, pyrolytic products of aconitine and a new alkaloid have been carried out to determine their functional groups.

#### VI. SYNTHETIC CRYSTALS

The "Know-how" of the Verneuil technique has been worked out for the commercial production of "A" quality, crack-free boules of sapphire, ruby, and of thin rod single crystals of sapphire, 15 cm. long and 1.5 - 4 mm. thick. A photo-electric device has been incorporated for an automatic control of the process. The dependence of the colour of the ruby on the concentration of  $\text{Cr}_2\text{O}_3$  and temperature has been investigated.

Final reports on (i) 'The Prospects of a Synthetic Gemstone Industry in India', and (ii) 'Technical observations on the Verneuil process' have been prepared.

#### VII. ZONE-FUSION TECHNIQUE

The technique is being used for the separation of difficultly resolvable mixtures and for the preparation of pure single crystals. A generalised equation has been deduced for determining the concentration of a solute along the length of the charge after a series of zone passes. Mixtures of (a) lead-tin, (b) naphthalene- $\beta$ -naphthol, and (c) thallous nitrate-potassium nitrate have been studied by the normal segregation method. The distribution results in (a) and (c) did not tally with those expected theoretically.

An infra-red spectroscopic method has been standardised for the analysis of mixtures of organic compounds.

#### VIII. LIGHT-SCATTERING BY AND FLOW PROPERTIES OF MACROMOLECULES

Light scattering and viscosity measurements have been undertaken to determine the size, shape, molecular weight and



flexibility of several polymers. It was found that sol-rubber showed different molecular weight in different solvents presumably due to an interaction with the solvent in the presence of light. Studies are in progress on the quantitative evaluation of parameters related to polymer-solvent interaction, and various polymethylmethacrylate fractions are being investigated in this connection. Interaction between several non-ionic and ionic surface active agents are being studied to find out the effect of charge on a particle on its light scattering properties.

Studies on Knox-gelatine, in 0.665% urea, showed that the gelatine in low concentrations remained molecularly dispersed. Based on this observation, molecular weights have been determined of several samples of trypsin treated transfusable gelatine prepared in the Biochemistry Division.

Following the theory of rate processes an equation for viscosity of a dilute polymer solution was deduced and reported last year. It has now been modified to give a more accurate value for the intrinsic viscosity. This shows better agreement with experimental data.

#### IX. METAL-PROTEIN INTERACTION

The interactions of Cu, Zn, Cd, and Co ions with bovine serum albumin and its derivatives have been studied by equilibrium dialysis, polarographic, optical absorption and electrophoretic mobility methods in an acetate buffer (pH 6.5; ionic strength 0.20). The results have been interpreted in terms of a competition between metal and hydrogen ions for the same functional group sites of the serum albumin molecule. The binding data obtained from the various methods have been collated and they lead generally to the same conclusions.

The affinity of bovine-serum-albumins has been found to decrease in the order - acetylated protein  $\rightarrow$  native protein  $\rightarrow$  esterified protein - for a given metal ion, and in the order

$\text{Cu}^{++} \rightarrow \text{Zn}^{++} \rightarrow \text{Cd}^{++} \rightarrow \text{Co}^{++}$  - for a given protein. Electrophoretic mobility data showed that  $\text{Co}^{++}$  ions were bound through carboxyl groups of the protein molecule, while  $\text{Cu}^{++}$ ,  $\text{Zn}^{++}$  and  $\text{Cd}^{++}$  ions were bound principally through the imidazole groups, the carboxyl groups contributed to the binding when more and more metal ions were bound, their effect decreasing in the order  $\text{Cd} \rightarrow \text{Zn} \rightarrow \text{Cu}$ .

It has been shown that the intrinsic association constant of the imidazole groups decreased with increase in the number of metal ions bound by the protein. The availability of these groups for reaction with the  $\text{Mg}^{++}$  ion decreases in the order  $\text{Cu} \rightarrow \text{Zn} \rightarrow \text{Cd}$ .

#### X. RARE EARTH METALLURGY

The electrolysis of  $\text{KThF}_5$  in fused  $\text{NaCl-KCl}$  mixtures was studied at  $750^\circ\text{C}$ . It was found that the thorium metal produced was contaminated with some  $\text{ThO}_2$ . Conditions for the electrolytic production of pure thorium are being worked out.

#### XI. PREPARATION OF WATER DISPERSIBLE D.D.T. (I.C.M.R. SCHEME)

Cheap water dispersible D.D.T. formulations containing 70-90% D.D.T. in the form of oil-bound and aqueous pastes have been successfully developed. The suspensibility, covering power and toxicity of these formulations are much better than those of the available commercial products.

Contact angle and sedimentation volume and rate measurements have been carried out with D.D.T., Dieldrin, Aldrin, and Endrin to select the most suitable wetting agents. Similar studies with Gammaxane and D.D.T. - Gammaxane mixtures are in progress.

Preliminary work has been undertaken on the preparation of dry wettable powders by spray atomization of mixtures of molten D.D.T. and suitable wetting agents. Addition of nucleating agents was found necessary for proper crystallization of D.D.T.

## XII. INSTRUMENTATION

Several transformers, d.c. sources, thermostat controls, resistance thermometers, etc. required by various divisions of the Laboratory were designed and constructed in addition to the routine maintenance and repair of a large number of laboratory instruments. The following special equipments were designed and constructed:

1. 100 k.v. High tension source for the Electron Diffraction Cameras
2. Focussing coil with electronic d.c. source and control panel for the new Electron Diffraction Camera
3. Complete X-ray diffraction unit
4. Electronic photo-electric control for the Verneuil Furnace
5. a new specimen carrier for electron diffraction camera incorporating a device for protecting vacuum joints by an intervening low vacuum zone which efficiently maintains high vacuum inside.
6. A potential divider for testing the high tension voltage and ripple in the electron microscope
7. Accessories for the light scattering apparatus, for the determination of reflectivity and transmissivity of evaporated metal films.

## XIII. SERVICES RENDERED

1. Infra-red absorption spectral analyses were undertaken for 6 outside laboratories

2. Identification analyses of the following samples were carried out by X-ray and Electron Diffraction techniques:

- (a) Several clays from Bhakra-Nangal project sites
- (b) Hard chromium plated piston rings from C.E.C.R.I., Karaikudi
- (c) Gun-cotton and nitro-cellulose from the Institute of Armament Studies, Kirkee.

3. Particle size measurements have been undertaken of gummy deposit in crankshaft casing in oil engines, and press-muds from different filtering processes, for M/s Kirloskar Oil Engines Ltd., Kirkee.

PLASTICS & POLYMERS DIVISION

I. FUNDAMENTAL STUDIES IN HIGH POLYMERS

(a) Copolymerisation studies

(i) The effect of temperature on the monomer reactivity ratios in copolymerization has been studied on two systems (1) methyl methacrylate - acrylonitrile (2) methyl acrylate-allyl chloride. The reactivity ratios were determined with the help of a new statistical computation procedure developed in this Laboratory and it was finally confirmed that differences in the heats of activation and not so much the entropies are responsible in influencing the copolymer composition.

(ii) With a view to studying the effect of the size of the ester groups on the reactivities of vinyl esters in copolymerization, three series of esters - acrylic, methacrylic and vinyl - were studied with allyl chloride as a co-monomer.

(b) Solution properties

(i) A study of the solution properties of polymethyl methacrylate, polymerized in bulk at different temperatures, suggests that during polymerization, successive monomeric units add in a random manner so as to introduce 'isomeric' structural changes in the internal architecture of the macromolecules accompanied by their improved solution properties.

(ii) Solution behaviour of different fractions of polyvinyl acetate polymerized in bulk at 40°C, has been studied in benzene under different shear rates. The effect of gradient on the various physical constant has been determined.

II. POLYSTYRENE

The suspension polymerization technique for producing polystyrene was studied in some detail to standardise the conditions of preparation of this polymer in the Laboratory. The samples obtained by altering the different reaction variables were studied for evaluating the efficiency of the technique.

a one gallon kettle for producing large batches of the polymer has been designed and fabricated. The quality of the final product is being compared with that of commercially available samples.

### III. ION-EXCHANGE

#### (a) Catalysis

Inversion of sucrose and the iodination of acetone have been investigated. The ion-exchange resins have been found useful for this purpose.

#### (b) Diffusion

Using the radioactive tracer technique the self diffusion of Rubidium into Amberlite IRC-50 has been studied. With two cation-exchange membranes the effect of ionic size and charge on the Donnan diffusion of chloride ion has been studied.

#### (c) Molecular sorption

The sorption of phenol on two different cation-exchange resins was studied in detail. The desorption phenomenon was also investigated and the results have been published.

#### (d) Preparation of cation-exchange resins

Starting from the commercial sample of cashew nutshell liquid an intermediate polymer for use in the synthesis of a suitable cation-exchange resin has been produced by reaction with formalin under acidic conditions. Work is in progress for preparing the cation-exchange resin in large quantities.

#### (e) Water softening

(i) A small water softening unit has been constructed and the resin employed is the cation-exchange resin prepared from cashew nutshell liquid. The unit has been successfully used for softening the Laboratory tap water.

(ii) The above unit has been used to feed softened water to a Mancsty Still. The complete unit for producing distilled water has been installed and operated successfully. Reproducible results have been obtained. The formation of

scales in the Manesty Still has been overcome by using the softened water.

#### IV. RUBBER

##### (a) Hydrochlorination

A detailed study has been made of the hydrochlorination of natural rubber latex and the various factors have been examined. It has been shown that complete cyclisation precedes hydrochlorination. The results show that the hydrochlorination reaction cannot be used as a tool to determine the degree of unsaturation in rubber and rubber derivative.

##### (b) Infra-red studies of cyclised rubber

The changes in chemical structure following cyclisation of rubber latex have been studied by means of infra-red absorption spectroscopy. A new method has been developed for determining unsaturation in cyclised rubber.

#### V. BATTERY CONTAINERS AND HONEYCOMB STRUCTURES

##### (a) Battery containers

Utilising indigenous asbestos a moulding composition has been standardised for use in preparing suitable battery containers. This composition has been tried at factory level and found quite efficient.

##### (b) Honeycomb structures

With a view to preparing suitable honeycomb structures for use in lamination a number of adhesives have been studied. A continuous strip gluing machine has been designed and fabricated.

#### VI. MISCELLANEOUS

(a) An adhesive tape machine has been designed and constructed. Trial runs are being conducted to standardise the various factors.

(b) Splitting of mica scrap sheets has been studied both by thermal and chemical means. Various binding agents have been investigated for preparing sheet mica (integrated) from scrap mica.

## RADIOACTIVE TRACER LABORATORY

The Tracer Laboratory is handling a wide range of problems of both applied and fundamental interest and is actively assisting other divisions of the Laboratory. Its contributions during the period under review are as follows:

### I. PERMEABILITY OF PAINTS AND VARNISHES (in collaboration with the Oils and Fats Section)

A new technique of rapid determinations of permeability of paint and varnish films, developed in this Laboratory, was further extended, with various isotopes to the study of the permeability of paint films intended for food containers and baked samples. A tracer method has been developed for simultaneous measurement of the film thickness.

### II. DIFFUSION IN SOLID STATE (in collaboration with Physical Chemistry Division)

Study of the migration of trace impurities in matrix of a host lattice is continued and has been extended to the CS-KCl system using CS-137. Results of fundamental interest have been obtained.

### III. BIOSYNTHESIS OF C-14 LABELLED COMPOUNDS (in collaboration with the Biochemistry Division)

Work for the development of an improved method for the synthesis of uniformly labelled carbohydrates photosynthetically, using radioactive  $\text{CO}_2$ , has been completed successfully. Chemical synthesis of positionally labelled sugars has been undertaken. A rapid, accurate and reproducible method for the assay of C-14 containing compounds developed in this Laboratory has been employed.

### IV. CARBOHYDRATE METABOLISM IN CITRIC ACID FERMENTATION (in collaboration with the Biochemistry Division)

Role of  $\text{CO}_2$  in the production of citric acid by *Aspergillus niger* was investigated and the following conclusions have been drawn from the studies using  $\text{C}^{14}\text{O}_2$ .

- (i)  $\text{CO}_2$  incorporation increases the yield of citrate
- (ii) the sp. activity of citrate is of the same order irrespective of the yield and
- (iii) the rate of  $\text{CO}_2$  participation in the synthesis of citrate depends on the age and the activity of the mould.

Work is being done using labelled glucose, to explore the alternative metabolic pathways of carbohydrate utilisation by *A.niger* leading to citric acid.

. EFFECT OF RADIATIONS IN MICRO-ORGANISMS  
(in collaboration with the Biochemistry Division)

Studies on the effects of radiations on micro-organisms was started with a view to develop mutants with improved characteristics for use in industrial fermentation. The irradiation was carried out with Y-90 on *saccharomyces cervisiae*.

Attempts are being made to obtain a mutant which does not revert. Experiments with *A.niger* have been undertaken with a view to obtain a mutant less sensitive to trace impurity. The Ra-Be neutron source is being employed for irradiation.

VI. DIAGNOSTIC STUDIES OF THYROID FUNCTION USING I-131  
(in collaboration with the Armed Forces Medical College)

Since no diagnostic tests (with radioactive iodine) for thyroid function are reported for Indian conditions, work was undertaken with the object of collecting data for hypothyroid, normal and hyperthyroid human beings. Initial tests were carried out on volunteers who were normal and these studies were extended to known hyper-thyroid and hypothyroid patients. The values so obtained were utilised for the diagnosis of thyroid abnormality in patients from local hospitals. The work will be continued using improved counting techniques.

VII. SELF-DIFFUSION OF IONS IN AQUEOUS SOLUTIONS

Work has been undertaken to determine the self-diffusion coefficients of various ions in solutions using radioactive isotopes. The effects of crystalline nature of solvent, the hydration of ions, the ion size, valence, di-electric constant,



temperature and concentration are being studied.

#### VIII. INSTALLATION OF RA-BE NEUTRON SOURCE

A 100 mc Ra-Be neutron source was installed in a separate room equipped with remote handling facilities, designed and fabricated here. The neutron source can be used in paraffin or water moderator and also in an irradiation chamber for work with gamma-radiations.

The problems at hand with the neutron source are:

- (i) effect of radiation on polymerisation (in collaboration with Physical Chemistry Division)

A study of the nature and mechanism of polymeric changes on irradiation has been undertaken.

- (ii) Mutation of micro-organisms with gamma and neutron irradiation (in collaboration with Biochemistry Division).

#### SURVEY & INFORMATION DIVISION

Work, carried out in the Division, during the year under review, may briefly be considered under following heads:

- I. Information service
- II. Industrial problems
- III. Small-scale chemical industries
- IV. Monographs on industrial subjects
- V. Services for other divisions (photographic and draftsmanship, etc.)

##### I. INFORMATION SERVICE

An important function of the Division (as laid down in the programme for the year) is to provide:-

(a) Scientific and technical information required by industry, and (b) information regarding the work conducted in the Laboratory to the offices of CSIR; and other Govt. departments.

Following is a summary of the work that was carried out in connection with these assignments:

(a) Technical enquiries

1342 enquiries on technical subjects were attended to during the year. Largest number was from manufacturers, seeking advice regarding details of manufacturing processes.

Following figures should give an idea of the nature of the technical enquiries that were attended to:-

1. Details of manufacturing processes	370
2. Small-scale industries	328
3. Details of chemical processes	222
4. Commercial information regarding availability of raw materials, plants and machinery	111
5. Utilisation of industrial wastes	30
6. Details for analytical processes	40
7. Academic subjects	61
8. Miscellaneous (unclassified)	180
	1342

A significant feature of this work was that quite a number of enquirers, who asked for information in previous years, approached again for information this year.

(b) Enquiries regarding work conducted at N.C.L.

84 enquiries regarding work conducted at N.C.L., were attended to. 33 detailed reports regarding the work conducted at the Laboratory were prepared and supplied to the Publication Division, C.S.I.R., Ministry of N.R. & S.R. and other Government organisations.

## II. INDUSTRIAL PROBLEMS

In case of certain technical enquiries it was necessary to carry out laboratory work before a reply was drafted. Problems thus arose in connection with the enquiries, and were taken up in the laboratory. Results of the investigations were communicated to the parties concerned.

During the year under review, two patent applications were filed on 'Process for utilisation of waste films'. Work in this connection was taken up on an enquiry for utilisation of waste cinematographic films, referred by the Ministry of Information and Broadcasting, Bombay.

(1) Furfural from some Indian gums

Six enquiries were received asking for details of a process for manufacture of furfural. Grain-husks, corn-cobs, and bagasse are well known sources for furfural. In view of the special interest shown by the manufacturers, investigations were taken up with a view to find if furfural could be obtained from other indigenous materials.

Investigations, carried out so far, show that some indian gums may prove very rich sources. Eight gums were investigated. Maximum yield was estimated in case of ghatigum, obtained from *Anogeissu latifolia* (28.2% on dry basis). Other gums which yielded furfural in good yields are summarised below:

<u>Gum</u>	<u>Furfural estimated by A.O.A.C. method (dry basis)</u>
Siris gum	16.5%
Gum acacia, B.P.	20.1%
Karaya gum	12.2%

(2) Utilisation of waste cinematographic films

Work on metallisation of washed films, reported earlier, was continued. A process has been worked out in which chemically deposited silver coat on the film is recoated with metals like copper, silver, or nickel, by means of electrodeposition. These metallized films take a high gloss on the surface and can be used as plastic mirror strips. Embroidery articles with high gloss, sequins, and 'tuccas' may also be prepared from metallized strips. A patent application has been filed for the above process (Ind. Pat. 55172).

Attempts have also been made to prepare cellulose ester moulding powder from waste films.

(3) Utilisation of safflower seed husk

Safflower seeds are dehusked prior to pressing in village ghanis. Large quantities of the husk accumulate in certain villages. A sample of the husk was received from Village Industries Co-operative with a request to find out some use for this material.

It was found that the husk can be converted into low grade activated carbon, which may find extensive use in refining sugar juices, vegetable oils, etc.

(4) Preparation of varnishes from cashew nutshell liquid

Certain firms had asked for suggestions to improve upon enamels and varnishes, prepared from resinols, obtained from Bhilawan and Cashew nutshell liquids. Investigations on cashew nutshell liquids were taken up in this connection.

Cashew nutshell liquid (C.N.S.L.) was copolymerized with linseed oil in different proportions at elevated temperatures in ordinary as well as CO<sub>2</sub> atmospheres. Lacquers and ester gum varnishes were prepared with the copolymer. Films of the lacquers and varnishes, applied by spreading on a glass plate dry in air within 24 hours. The ester gum varnish prepared as above, showed better water resistance than the ester gum linseed oil varnish.

(5) Reactivation of used activated carbon

A firm wanted to be advised about methods, that may be followed for reactivating stocks of used activated carbons. Their samples were tested, treated with acids, heated in closed retorts, washed and finally dried. Thus reactivated, the samples showed an activity about 24% lesser to that of the original carbon. Details of the process have been communicated to the party concerned.

### III. SMALL-SCALE INDUSTRIES

363 enquiries were attended to during the year. 68 parties approached personally for discussion or for demonstrations, and were attended to.

32 typed copies of monographs on various small-scale industries prepared in the Division were supplied on request to Institutes for small industries, Directorates of Industries in various States, and other Government organisations.

#### IV. MONOGRAPHS ON INDUSTRIAL SUBJECTS

Subjects on which repeated enquiries were received were studied in detail and information regarding market position, availability of raw materials, details of manufacturing processes, technical applications, and approximate cost of manufacture was compiled in form of small monographs.

Seven monographs on subjects noted below were compiled during the year under review.

1. Manufacture of soda silicate
2. Manufacture of soda sulphide
3. Manufacture of washing soap
4. Manufacture of boot polish
5. Manufacture of matches (Small-scale industry)
6. Manufacture of ether
7. Refining of used lubricating oils

#### V. OTHER SERVICES

927 photographs (including prints and enlargements) 29 lantern slides, and 364 drawings (including 237 blue prints) were supplied.

30 charts (30" x 20") depicting flow-sheets of research projects completed in the Laboratory were prepared for Exhibition in Indian Industries Fair held in Delhi in November-December, 1955.

#### LIBRARY

2071 new books including bound volumes of periodicals, 37 microfilms, 42 patents and 5 photocopies were added to the Library during the year under review.

Amongst the publications added to the Library, 308 books including a selection of books from the Brookhaven National Laboratory, Upton, New York and United States Information Services Library, Bombay, were received as donation.

The Library issued 5984 publications on loan. 9575 readers used the Library.

WORKSHOP

Total number of job cards received	2291
Total number of job cards completed	2370
Arrears completed	79

Some of the major and precision equipment/apparatus designed and fabricated, are mentioned below:

1. Photo-synthetic chamber of perspex sheet material for the Biochemistry Division
2. Slide carrier for X-ray unit for the Physical Chemistry Division
3. One electric furnace with thermostatic control & device for the Plastics & Polymers Division
4. One electric muffle furnace for the Radioactive Tracer Laboratory
5. One Electron Diffraction camera for the Physical Chemistry Division
6. Boosters erection work for the supply of pressure water system to the Laboratory
7. Erection & installation of services to air conditioning units (3 Nos.)
8. One pole-piece of very high precision for electron microscope for the Physical Chemistry Division
9. Two remote control pipettes for handling radioactive samples
10. Remote control mechanism for neutron source in the Radioactive Tracer Laboratory

CIVIL WORK

1. Retaining wall along the road leading to the animal house completed
2. Partition wall 18" thick in the Radioactive Tracer Laboratory completed
3. Pucca drain along the road side completed
4. Water proof cement painting of the cascade ponds completed

WORKS COMPLETED THROUGH CONTRACTORS

1. Construction of the gelatine pilot-plant shed
2. Shed for the boiler and the foundry
3. Deepening of well No.3
4. Distemper of the cafeteria and painting wood work.

PAPERS PUBLISHED DURING 1955-56

1. Bedekar, S.G., Properties of sodium carbonate-bicarbonate solutions; J. appl. Chem., 5 (1955), 72.
2. Sarma, B. & Gupta, J., Spectrophotometric determination of tantalum; J. Ind. Chem. Soc., 32 (1955), 285.
3. Damodaran, V., & Gupta, J., Titanium dioxide from bauxite sludge; J. sci. industr. Res., 14 (1955), 292.
4. Thakar, K.R., Raw Materials of Radio (Electronics) Industry: Part II, Radio Services, 17, No.4 (1955), 10.
5. Rajan, K.S., and Gupta, J., Separation of zirconium and hafnium using anion exchange resin - Part I; Qualitative studies, J. sci. industr. Res., 14B, (1955), 453.
6. Doraiswamy, L.K., and Pai, M.U., Behaviour of active carbons in the catalytic dehydro-chlorination of ethylene dichloride to vinyl chloride; J. sci. industr. Res., Vol. 15B, No.2 (1956), 87-93.
7. Bijawat, H.C. and Sarma, P.K., The influence of humidity and temperature on the stability of bleaching powder, J. App. Chem. Vol. 6, (1956), 60-67.
8. Kapadia, V.H., and Aggarwal, J.S., Stabilization of kamala seed oil, J. sci. industr. Res., 14B, (1955), 186.
9. Kulkarni, A.B., and Merchant, J.R., Anthoxanthins; Part II: Identification of the degradation products of anthoxanthins by paper chromatography; J. sci. industr. Res., 14B, (1955), 153.
10. Pathak, K.D., and Aggarwal, J.S., Fractionation of oil fatty acids by urea-complexes method, - separation of erucic acid; J. sci. industr. Res., 14B, (1955), 231.
11. Bholanath: A study of the infra-red spectra of aconitine delphinine and their alkalines; J. Indian Chem. Soc., 32 (1955), 75.
12. Shah, L.G. (Mrs.), Shah, G.D., and Shah, R.C., Borontrifluoride as a new condensing agent in the pochnann reaction, J. Indian Chem. Soc., 32 (1955), 302.
13. Kulkarni, A.B., and Shah, R.C., Studies in the aromatic sulphonyl chlorides, Part III: action of chloro-sulphonic acid on toluene and toluene sulphonyl chlorides - J. Indian. Chem. Soc., (Ind. and News Edition), 18 (1955), 22.
14. Chakravarty, K.K., and Bhattacharyya, S.C., Cinnamyl alcohol, J. Indian Chem. Soc. (Ind. and News Edition) 18 (1955), 31.
15. Shah, R.C., Kulkarni, A.B., and Thakar, V.M., Pristinerin Part I, J. Chem. Soc., (London), (1955), 2515.

16. Bose, J.L., and Chandran, K., Oestrogenic activity of the fixed oil of chana (*Cicer arietinum* Linn), J. sci. industr. Res., 14C, (1955), 128.
17. Shah, V.R., Joshi, C.G., and Kulkarni, A.B., Synthesis of fustin trimethyl ether and dihydrorobinetin tetramethyl ether, Chemistry and Industry, (1955), 1062.
18. Dutta, N.L., Chemical examination of *Mundulea suberosa* Benth, J. sci. industr. Res., 14B, (1955), 424.
19. Subbaratnam, A.V., Chemical examination of the bark of *tabernaemontana heyneana* wall, J. sci. industr. Res., 14B, (1955), 424.
20. Mitra, C.R., A note on chemical examination of the oil from *calophyllum inophyllum* Linn, J. sci. industr. Res., 14B, (1955), 481.
21. Aggarwal, J.S., Kamala seed oil, J. sci. of Food & Agri.(London), 6 (1955), 364.
22. Sethi, S.C., and Aggarwal, J.S., Utilization of cashew kernel rejection, Oil & Oilseeds J., 8 (1955), 5.
23. Grover, P.K., Shah, G.D., and Shah, R.C., Studies in xanthenes; Part IV, A new and convenient synthesis of hydroxyxanthenes, J. Chem. Soc., (1955), 3982.
24. Shah, L.G.(Mrs.), Shah, G.D., and Shah, R.C., A note on the synthesis of geijerin, J. sci. industr. Res., 14B, (1955), 670.
25. Chakravarti, K.K., and Bhattacharyya, S.C., Chemical examination of Indian spearmint oil, Part II: Elucidation of the structure of mint glyoxal, Perf. Essential Oil Rec., 46 (1955), 256.
26. Chakravarty, K.K., Dasgupta, S.(Mrs.), and Bhattacharyya, S.C., Infra-red spectra of compounds containing a cyclopropane ring, Perf. Essential Oil Rec., 46 (1955), 330.
27. Chakravarti, K.K., and Bhattacharyya, S.C., Oxidation of carvone and citronellal with selenium dioxide, Perf. Essential Oil Rec., 46 (1955), 341.
28. Chakravarti, K.K., and Bhattacharyya, S.C., Chemical examination of the oil of Malabar lemongrass, Part II, Perf. Essential Oil Rec., 46, (1955), 365.
29. Dasgupta, S.(Mrs.) and Aggarwal, J.S., Infra-red studies on the isomers of kamalolenic acid, J. Am. Oil Chem. Soc., 32, (1955), 501.
30. Nair, C.K.N., Sharma, P.G. and Aggarwal, J.S., A radioactive isotope study of the permeability of paint and varnish films, J. sci. industr. Res., 14B, (1955), 549.
31. Varma, J.P., Bhola Nath and Aggarwal, J.S., Structure of sterculic acid, *Nature*, 176 (1955) 1082.



32. Sethi, S.C. and Aggarwal, J.S., Stabilization of edible fats by spices, Part II, A new antioxidant from betel leaf, J. sci. industr. Res., 15B, (1956), 34.
33. Sogani, N.C., and Bhattacharyya, S.C., 3-Hydroxy-1:3-diphenyl triazine as reagent for palladium - Ann. Chem. 28, (1956), 81.
34. Shah, G.D., and Shah, L.G. (Mrs.), Separation of  $\gamma$ -resorcylic acid from a mixture of  $\beta$ - and  $\gamma$ -resorcylic acids, J. sci. industr. Res., 15B, (1956), 159.
35. Kulkarni, A.B., and Joshi, C.G., Synthesis of the third racemate of flavan-3:4-diol, Chem. and Ind. (1956), 124.
36. Pathak, K.D., and Aggarwal, J.S., A general method for the acetylation of hydroxy fatty acids and their glycerides, J. sci. industr. Res., 14B, (1955), 637.
37. Gupta, A.S., and Aggarwal, J.S., Separation of methyl esters of fatty acids from their mixtures by urea complexes, J. Indian Chem. Soc., 33, (1956), 197.
38. Rao, N.V.C., Determination of unsaturation in cyclised rubber using phenyliododichloride, Die Makromolekulare Chemie, Vol. XVI, Part 3, (1955), 195-203.
39. Gadkary, S.D., and Kapur, S.L., Chain transfer in solution polymerization III, Methyl Acrylate, Die Makromolekulare Chemie, Vol. XVII, Part I, (1955), 29-38.
40. Pande, J.B., Ramakrishnan, C.S., Raghunath, D., and Kapur, S.L., Interdiffusion between rubber solvents under static conditions, Ibid, Vol. XVI, Part 3, (1955), 204-12.
41. Sharda Dasgupta, Pande, J.B., and Ramakrishnan, C.S., Infra-red studies on natural rubber and aged natural rubber, J. Poly. Sci., Vol. XVII, (1955), 255-262.
42. Shah, H.A., and Govindan, K.P., Ion exchangers, Part IV, Operating characteristics of some cation exchange resins, J. sci. industr. Res., 14B, (1955), No.5, 222-229.
43. Bafna, S.L., Catalysis by ion exchange resins, Acetone iodine reactions, J. Phys. Chem., 59, (1955), 1199.
44. Bafna, S.L., and Govindan, K.P., Molecular sorption on ion exchange resins, Industrial & Engineering Chemistry, Vol. 48, No.2 (1956), 310-317.
45. Ramakrishnan, C.S., Sharda Dasgupta, and Rao, N.V.C., Infra-red absorption studies of cyclized rubber and chlorinated cyclized-rubber, Die Makromolekulare Chemie, Vol. XX, Pt.I, (1956), 46-56.
46. Rao, N.V.C., and Raghunath, D., Preparation of Factice: A new use for tobacco and safflower seed oils, J. sci. industr. Res., 14B, (1955), 425.

47. Krishnaswamy, N., Effect of ionic size, charge and valency on Donnan Diffusion in cation-exchange membrane, Current Science, 24, (1955), 234.
48. Ramakrishnan, C.S., and Pandey, J.B., Diffusion with Multiple zones of interaction, Current Science, 24, (1955), 302.
49. Nair, C.K.N., Govindan, K.P., and Bafna, S.L., Self diffusion of  $Rb^+$  in and through cation-exchange resins - J. sci. industr. Res., 14B, (1955), 478.
50. Kapadia, F.H., Adsorption and anomalous viscosities, Die Makromolekulare Chemie, Vol.XVI, Part 3, (1955), 238.
51. Joshi, R.M., The penultimate unit effect in free radical copolymerisation, J. Poly. Sci., Vol.XVII, No.83, (1955)
52. Ramakrishnan, C.S., Sharda Dasgupta, and Pandey, J.B., Infra-red studies on chlorinated rubbers, J. Poly. Sci. Vol. XIX (1956), 323-330.
53. Krishnaswamy, N., Progress in the electrochemical studies of ion-exchange resins and membranes, J. sci. industr. Res., Vol.14A, (1955), 235-40.
54. Vaidya, M.R., Kapur, S.L., Polystyrene, a review; Paintindia, Vol. V, No.3 (1955), 23-26.
55. Kapur, S.L., Recent developments in Plastics, Paintindia, Vol.V, No.4 (1955), 13.
56. Kapur, S.L., Recent developments in Polyethylene, Paintindia, Vol. V, No.8 (1955), 23-25.
57. Joshi, R.M., Kapur, S.L., Reactivity constants in copolymerization, J. Poly. Sci., Vol.XIX, No.93, (1956), 582-83.
58. Govindan, K.P., Krishnaswamy, N., and Kapur, S.L., Ion-exchange in cane sugar industry, 24th Proc. of Sugar Tech. Assn. of India (1955).
59. Banerjee, B.C., Goswami, A., an electron diffraction study of the structure of electro-deposited nickel, Part I, J. sci. industr. Res., 14B, (1955), 322.
60. Goswami, A., Nickel deposition without current - a rapid method of estimation of hypophosphite, J. Ind. Chem. Soc., (Ind. & News Ed.), 18, (1955), 116.
61. Sinha, K.P., and Dasgupta, A.K., Evaporation of trace impurities from the matrix of a host lattice, J. sci. industr. Res., 14B, (1955), 320.
62. Marathe, E.V., Half life of Yttrium-90, J. sci. industr. Res., 14B, (1955), 354.
63. Das Gupta, A.K., Nair, C.K.N., 'Counting of C-14 in the solid state', J. sci. industr. Res., 15B, ((1956), 1.
64. S. Dasgupta (Mrs.) and Bhola Nath, A study of the infra-red spectra of staphisine and a new alkaloid, J. Ind. Chem. Soc., 32, (1955), 767.

65. Goswami, A., and Trehan, Y.N., The thermal oxidation and reduction of a Copper(110) face, Trans. Faraday Soc., 52, (1956), 358.
66. Verma, J.P., Dasgupta, S., Bhola Nath, and Aggarwal, J.S. Infra-red studies of sterculic acid and some related compounds - J. Ind. Chem. Soc., 33, (1956), 111.
67. Danodaran, M., Govindarajan, V.S., and Subramanian, S.S., The proteolytic system of Bacillus Licheniformis Biochemica et Biophysica acta, 17, (1955), 99-110.
68. Danodaran, M., Jagannathan, V., and Kartar Singh, Carbohydrate metabolism in citric acid fermentation III - The variation in glycolytic enzyme content of A.niger during citric acid fermentation, Enzymologia 17, (1955), 199.
69. Danodaran, M., Sivaraman, C., and Dhavalikar, R.S., Amino acid composition of elastoidin, Biochemical Journal, 62, (1956), 621.
70. Sadana, J.C. & Jagannathan, V., Purification and properties of the hydrogenase Desulfovibrio desulphuricans, Biochemica et Biophysica acta, 19 (1956), 440.
71. Jagannathan, V., Kartar Singh, and Danodaran, M., Carbohydrate metabolism in citric acid fermentation, IV, Purification and properties of aldolase from A.niger - Biochemical Journal, 63 (1956), 94.
72. Kalra, S.L., and Gurdas Singh: Blood values of pariah dog population of Poona, Ind. J. Med. Science, 10, (1956), 460-61.
73. Gurdas Singh and S.L. Kalra: Dextravan and Intradex as plasma substitutes, Ind. J. Med. Res., 44, (1956), 333-39.

#### PAPERS COMMUNICATED FOR PUBLICATION

1. Gharpurey, M.K.: Epitaxial crystal growth in iron pyrites, cube and octahedral faces, Part I, Growth on cube face of pyrites, J. sci. industr. Res.
2. Gharpurey, M.K., Epitaxial growth on iron pyrites, cube and octahedral faces, Part II, Growth on octahedral face of pyrites, J. sci. industr. Res.
3. Goswami, A., Disorientation of single crystal substrate due to epitaxial stress, Proc. Phys. Soc.(London)
4. Goswami, A., On the mechanism of the change of orientation, J. sci. industr. Res.
5. Goswami, A., anodic oxidation of a copper(110) face in alkaline solution.
6. Verma, J.P., Dasgupta, S.(Mrs.), Bhola Nath and Aggarwal, J.S., The component acids of glycerides: composition of the oil of sterculia foetida Linn. J. Amer. Oil Chem. Soc.

7. Nanavati, D.D., Dasgupta, S.(Mrs), and Aggarwal, J.S., Estimation of iso-oleic acid in hydrogenated fats, J. Amer. Oil. Chem. Soc.
8. Jagannathan, V., Rangachari, P.N., and Damodaran, M., Carbohydrate metabolism in citric acid fermentation - V. Purification and properties of *zwischonferment* from *A.niger*, Biochemical Journal (1955).

#### PAPERS COMMUNICATED FOR DISCUSSION

1. Goswami, A., Studies on surface structure by Electron Diffraction, Indian Instt. of Metals, Annual Meeting(1955) Gharpurey, M.K.,
2. Doo, A.A., and Gharpurey, M.K., Electron Microscopy, Indian Instt. of Metals, Annual Meeting(1955)
3. Sinha, K.P., Theory and mechanism of solid-solid reactions, Symposium on 'Physics of the solid state' National Academy of Sciences, Allahabad (1955).
4. Goswami, A., Crystal growth in chemical displacement - Indian Science Congress (1956).
5. Rao, M.S.N., and Hiralal, The binding of zinc and cadmium ions by native and modified bovine serum albumins, Indian Science Congress (1956)

#### PATENTS FILED, ACCEPTED & SEALED DURING 1955-56

##### PATENTS FILED

1. Indian Patent 54,395: A process for the manufacture of active manganese dioxide suitable for dry batteries, U.C. Aggarwala, N.R. Sanjana, & J. Gupta.
2. Indian Patent 54,713: Extraction of fluorine in a soluble form from alkaline earth fluorides, M.M. Singh & J. Gupta.
3. Indian Patent 54,959: an electrical device for double-action on/off control - S.L. Sastry.
4. Indian patent 54,867: A process for the manufacture of nicotine sulphate from tobacco and tobacco wastes - H.C. Bijawat, R.K. Razdan and G.V. Potnis.
5. Indian patent 54,828: Process for the manufacture of triammonium phosphate - K. Seshadri, & J. Gupta.
6. Indian patent 54,829: Process for the manufacture of an ammonium phosphate fertiliser from triammonium phosphate K. Seshadri, & J. Gupta.
7. Indian patent 55,171: Treatment of anacardic material such as cashew nutshell liquid for use in electrical insulating varnishes - K.A. Thakar, & J. Gupta.
8. U.S. Patent 49,8426: a gelatin solution suitable for use as a plasma substitute - M. Damodaran & Gurdas Singh.

9. Indian patent 55,172: A process for the utilisation of waste cinematographic films - K.G. Mathur & A.M. Lele
10. Indian patent 55,546: Improvements in or relating to ion-exchange membrane - C.S. Ramakrishnan & N. Krishnaswamy.
11. Indian patent 55,504: A process for the preparation of long chain unsaturated ketones and 1- $\omega$ -ketodicarboxylic acids from the said ketones - K.K. Chakravarti and S.C. Bhattacharyya.
12. Indian patent 55,757: A process for the preparation of long chain unsaturated ketones and 1- $\omega$ -ketodicarboxylic acids from the said ketones - B. Menon, U.G. Naik, R.K. Razdan, K.K. Chakravarti & S.C. Bhattacharyya.
13. Indian patent 56,725: A new process for the purification of "selenium" - D.N. Sen & J. Gupta.
14. Indian patent 56,724: A water dispersible DDT paste, K.V.N. Rao, S.P. Bhide, S.B. Kulkarni, and A.B. Biswas.
15. Indian patent 56,726: A preparation of water dispersible D.D.T. as an oil bound paste - S.B. Kulkarni, A.B. Biswas K.V.N. Rao & S.P. Bhide.

#### PATENTS ACCEPTED

1. Brit. patent 20,835(1951): Air drying wrinkle finish coating compositions - J.S. Aggarwal, P.G. Sharma.
2. Indian patent 52,112: Improvements in or relating to cast synthetic resins - H.A. Shah.
3. Indian patent 53,636: Improvements in or relating to coating compositions - K.K. Sarin & S.L. Kapur.

#### PATENTS SEALED

1. Indian patent 52,027: Composition for preparing cylindrical rolls from washed safety base cinematographic films - K.G. Mathur & A.M. Lele.
2. Indian patent 49,364: The manufacture of adhesive tapes - N.V.C. Rao.
3. U.S. Patent 27,076,86: Production of moulding powder from shellac and bhillawan resins - S. Siddiqui, K.K. Sarin & J.P. Varma.
4. Indian patent 50,926: Manufacture of nicotinic acid - G.D. Shah & R.C. Shah.
5. Indian patent 53,414: Treatment of molasses to render it suitable for use in phenolic type moulding compositions - A. Ghosh.
6. Indian patent 52,801: A process for preparing a modified gelatin suitable for transfusion - M. Danodaran & Gurdas Singh.