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To my father, Who inspired me
for

This research work.

but who did not survive to see

The work complete.

S. S. Manavathi.
Aug. 1957.

16 SEP 1959

MODIFICATION OF NICKEL CATALYST FOR THE HYDROGENATION OF
VEGETABLE OILS

and

APPLICATION OF N-BROMOSUCCINIMIDE FOR THE CREATION OF
CONJUGATION IN FATTY ACIDS AND OILS.

A THESIS SUBMITTED TO

THE UNIVERSITY OF BOMBAY.

for

THE DEGREE OF MASTER OF SCIENCE



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NAN

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*

B.D. Anavati.

:: PRESENTATION ::

For the sake of clear exposition of the subject,
the thesis has been divided into two parts as follows:-

PART A: Modification of Nickel Catalyst for
the Hydrogenation of Vegetable Oils.

PART B: Application of N-Bromosuccinimide
for the creation of conjugation in
Fatty acids and oils.

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PART 4.

NICKEL CATALYST FOR THE HYDROGENATION OF VEGETABLE OILS:

The vanaspati industry is the second biggest food-processing industry in India. The country produces more than 2,60,000 tons of vanaspati every year. Besides satisfying the entire internal consumption, the material is also exported to United Kingdom and some other countries. In its manufacture, it is absolutely essential to avoid any considerable formation of saturated acids and to build up low temperature body, mostly through the formation of iso-oleic acids. These aconditions are only attained if the process of hydrogenation is of selective nature. The selective hydrogenation is also necessary for the stability characteristics of the product. Nickel in the form of formate is almost entirely employed for the preparation of catalyst for the hydrogenation of oils. The processes of manufacture of high grade type of catalyst from this salt are, however, kept secret and large quantities in the past and substantial amounts even at present are imported in the country. The method of the preparation of the unsupported nickel catalyst from the formate salt were first studied and the conditions of hydrogenation of some of the more important oils were determined. As a result of this work, the following conclusions were drawn.

1) The unsupported nickel catalyst prepared by the wet reduction process of the formate at 460° - 470° F has been found to give the hydrogenated product of maximum selectivity and desired consistency.

2) A hydrogenation temperature, 176° - 182° C and pressure, 85-90 p.s.i. with nickel concentration, 0.2 per cent on the weight of the oil has been found to give the desired product.

3) A highly unsaturated oil like linseed oil may not give a product of desired consistency.

4) The hydrogenation of oils containing materials which poison the catalyst such as mustard oil is better accomplished if a part of the catalyst is added first, removing it after sometime and adding the fresh catalyst again.

5) Out of the various oils studied for hydrogenation, groundnut and cottonseed oils were found quite satisfactory for vanaspati manufacture.

6) The re-usage of the spent catalyst may be limited to three or four batches of this oil. Even these batches may be mixed together in order to get a uniform product.

Various supports for the preparation of nickel catalysts were investigated. It has been found that a nickel catalyst supported on limited amounts of neutral carriers of the type hyflo-supercel or decolourising carbon (2:1) is preferable for increasing the rate of hydrogenation to the unsupported one.

As nickel formate has to be imported and also in view of the fact that an economic process has been developed in this laboratory for the recovery of nickel from spent hydrogenation catalyst in the form of its basic carbonate, hydroxide or sulphate, the utility of such cheaper salts of nickel as alternative to nickel formate for the preparation of the catalyst for vanaspati industry has been investigated. The basic carbonate of nickel prepared from the sulphate in concentrated solutions and supported on a neutral carrier such as hyflo-supercel when reduced under a moderate pressure of 100 p.s.i. at a temperature of 255-260°C by wet process gives a catalyst by the use of which a hydrogenated product of satisfactory consistency and selectivity can be obtained. The time of hydrogenation is, however, somewhat more than that required by the use of catalyst derived from nickel formate. It has also been found that if the precipitated basic carbonate of nickel before filtration is washed with a large amount of water continuously, a catalyst of improved quality is obtained.

The presence of some metals in small amounts in the nickel catalyst is known to promote the rate of hydrogenation of various oils and also influence the selectivity of the process. These catalysts, however, are prepared by dry-reduction process giving pyrophoric products which are not very suitable for the oil hardening industry. Some metals were co-precipitated with the basic carbonate of nickel and the catalysts from these salts prepared by wet reduction process under hydrogen pressure as given above. It was found that by this procedure excepting chromium,

silver and molybdenum, all the rest retarded the rate of hydrogenation of the oil. Some preliminary studies indicated that a process of continuous washing of the co-precipitated basic carbonate of nickel and chromium gave a catalyst which almost compared in its property to that obtained from the formate salt.

While the above work was in progress, a search was made to find an easy and accurate laboratory method for the estimation of trans-isooleic acids in the hydrogenated fats, as an alternative to the infra-red spectrophotometric method, the equipment for which is not always available. As a result of analysis of a large number of samples of hydrogenated fats, it has been found that the Twitchell lead salt alcohol procedure as modified by Cocks, Christian, Harding (Analyst, 1931, Vol. 56, pp. 368) may be recommended as an alternative procedure for the determination of trans-iso-oleic acids in the hydrogenated fats, where a more accurate infra-red procedure is not available.

PART B.

APPLICATION OF N-BROMOSUCCINIMIDE IN THE PRODUCTION OF CONJUGATION IN FATTY-ACIDS AND OILS.

Ziegler and his co-workers have shown that a hydrogen atom on a methylene group adjacent to an ethylenic double bond may easily be replaced with bromine by means of N-bromosuccinimide. Beyond an attempt by Teeter to introduce bromine in the allylic position in methyl esters of soybean fatty acids and methyl linoleate and Schmid and Lehmann to brominate methyl elaidate and methyl brassidate, little is

^{-ed}
report_λ in the literature on the application of
N-bromosuccinimide to fats and their fatty acids.

In this thesis, studies on the allylic bromination of methyl esters of oleic, petroselinic and erucic acids with N-bromosuccinimide have been carried out. The thermal dehydrobromination of the products have led to the syntheses of the corresponding conjugated fatty acids (yields 30-40%). Bromination of these acids with equimolecular proportions of N-bromosuccinimide leads to the substitution of bromine in the allylic position at the carbon atom farther from the carboxyl group. Similar treatment of stearolic and behenolic acids with N-bromosuccinimide followed by thermal dehydrobromination results in the introduction of a double bond in conjugated position to the triple bond initially present. The excess of N-bromosuccinimide with mono-ethenoid acids and subsequent thermal dehydrobromination gives a mixture of diene and triene conjugated acids.

This work was extended to 9:12-linoleic acid. Parallel experiments with the di-ethenoid acid resulted in a mixture of fatty acids having diene, triene, and tetraene conjugated double bonds.

When the process was applied to glyceride oils like mustard, groundnut, olive, karanja, neem, tobacco and safflower oils, the thermal dehydrobromination was found to lead to gelation and the treatment was consequently carried out successfully by the use of pyridine, quinoline or 2:4:6-

collidine. The conjugation has been characterised by the measurement of ultra-violet absorption spectra, iodine number and diene value. The film of all the treated oils dried in wrinkled patterns.

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PART A.

MODIFICATION OF NICKEL CATALYST FOR THE HYDROGENATION
OF VEGETABLE OILS.

I_N_T_R_O_D_U_C_T_I_O_N.

ROLE OF CATALYST IN THE HYDROGENATION OF OILS.

THE IMPORTANCE OF NICKEL CATALYST.

Importance of hydrogenation:

Hardening of vegetable and marine oils by means of catalytic addition of hydrogen to the ethylenic linkages is a process of great significance in modern oil and fat technology. The process has proved of much economic and technical importance. In this process, the properties of glyceride oils are modified in such a way that their edible characteristics remain unimpaired. The hydrogenated oils are purer and more stable than liquid raw oils. They possess definite desirable properties and have attractive appearance.

Hydrogenation serves the primary objective of converting the more plentiful liquid oils into plastic fat products like margarine, vanaspati and the various types of shortenings. Through this process, many oils and fats have become quite suitable for edible purposes. For instance, the large scale production of hydrogenated cotton seed and other vegetable oils have replaced expensive hog and beef fats in America and various European countries. Similarly vanaspati made from groundnut and cottonseed oils has become more or less a substitute for more expensive cow and buffalo ghee in India.

Hydrogenation is frequently employed for the improvement of the consistency or stability of vegetable oils and animal fats. The importance of the process has considerably increased during the last two or three decades.

Varieties of products for example large stearin, margarine, hydrogenated greases for soap making, etc. are manufactured by this process. It has also been extended in the manufacture for certain non-edible fat products, for example, artificial waxes, lubricants, etc. The process has helped, in particular, the soap industry. There the hydrogenated low grade oils have been employed. Moreover, this has enabled the release of costly oils like coconut oil, edible animal fats and drying oils for other purposes with the added advantage that the soap products are quite firm, free of rancidity and have desired properties.

In Industry, the course of hydrogenation is controlled to manufacture products having specific characteristics like melting point, plastic range, titre value, refractive index, etc., in accordance with the requirements of the trade.

Hydrogenation also serves another important objective of improving the keeping quality of edible oils. The process reduces the more unsaturated linkages which are susceptible to oxidation. Thus it improves the resistance of fats and oils to deterioration through oxidation, flavour reversion, or polymerisation. In the production of hydrogenated fats, many incidental benefits for example, the removal of colour, destruction of peroxides present in liquid oils, etc. are attained.

Hydrogenation brings about various changes in physical and chemical characteristics of glyceride oils. It changes the amount and nature of the fatty acid constituents of the oils, depending upon the conditions of hydrogenation such

as temperature, pressure, catalyst concentration, etc. The iodine value of the oil decreases as the hydrogenation proceeds and physical characteristics of the hydrogenated products like titre value, melting point, refractive index etc. are accordingly altered. The physical and chemical properties of the final product depend upon the types of glycerides formed. Further it may be added that these characteristics are affected by the isomerising influences accompanying the reaction which are essentially governed by the conditions of hydrogenation.

VANASPATI INDUSTRY IN INDIA.

The vanaspati industry in India is not very old when compared with sugar and textile industries. It started on a small scale after the world war; but it rapidly developed during and after the Second World War. In 1935, the production of vanaspati was 18,000 tons, in 1956 it reached a little over 3,50,000 tons. In other words, production increased twenty fold in the space of twenty years. To-day, next to the sugar industry, it is the largest food processing industry in India. Nearly Rs.25 crores have been invested into it. But so far the development of vanaspati industry has not given any impetus to the establishment of nickel catalyst industry in the country. In America and other European countries, its development was witnessed during the rapid growth of hydrogenation industry. The oil hardening industry in India consumes about 3,000 tons of nickel formate annually. But all this catalytic material is imported either in the form of ready made catalyst or as dihydrate formate salt. This results into a loss of foreign exchange of the value of rupees two crores. Much can be done if nickel formate is manufactured in India. This, however, does not seem to be

quite feasible in the near future because formic acid is not produced in the country.

The oil hydrogenation industry is of considerable significance in the context of the present shortage of food in the country. All these considerations therefore warrant a search for an alternative cheaper salt of nickel which can be utilized for the manufacture of nickel catalyst and can be prepared in the country.

NICKEL CATALYST FOR HYDROGENATION.

Hydrogenation began to be recognised as one of the major methods of chemical technique as early as 1897. This was due to the classical researches of Sabatier¹ and his co-workers on the process of hydrogenation in the vapour phase. This led to the general introduction of this method into industry and laboratory research.

Norman² later discovered that liquid marine and vegetable oils could be converted by this method into hard white fats. A year later the use of high pressure was introduced in the process of hydrogenation. This combined with the use of nickel catalyst has brought about a high state of development in the methods of hydrogenation.

Ellis³ reviewed the early work on hydrogenation catalysts in 1930. Since then nickel has become the pre-eminent catalytic metal without having any satisfactory substitute. Catalysts prepared from platinum or palladium are highly active, but unduly costly and platinum, in addition, yields products of less desirable characteristics than nickel⁴. In fact, no catalyst other than one based on nickel for

hydrogenation of ethylenic linkages in fats is available⁵. However, nickel catalysts are frequently promoted with other metals or metal oxides.

The hydrogenation system of glyceride oils with solid nickel catalyst is a typical example of heterogeneous catalysis. Nickel being a solid catalyst, it performs the catalytic function through the nature and extent of its surface. Hence the surface phenomenon or the catalyst structure has become extremely important in hydrogenation. The characteristics of nickel catalyst is determined by the sub-microscopic character of its surface⁶.

Nickel catalyst has got a definite influence upon the glyceride composition of the reaction products. Different nickel catalysts manufactured under diverse conditions give products of different glyceride composition. Thus activity and selectivity of nickel catalyst are its important properties to decide the course of hydrogenation. The selective nature of nickel catalyst plays an important role in the hydrogenation of oils and fats, where one catalyst may produce more iso-oleic acids than the other⁶.

SELECTIVITY IN HYDROGENATION

The term "selectivity" means the preferential saturation of the more highly unsaturated components to the less unsaturated ones. Thus the term "selectivity" has often been used to describe the preferential conversion of linoleic acid to oleic acid or its isomers in mixtures where the mixtures of both these unsaturated acids free or combined, are hydrogenated. After the whole of the linoleic acid is changed, the mono-ethenoid acid then gets converted to saturated acids.

During hydrogenation of oils containing oleic and/or polyethenoid acids, both positional and geometrical isomers of oleic acid and possibly also of linoleic acid are formed. Several investigators have established that both types of isomers are present in partially hydrogenated oils.

Bömer⁷ was the first to investigate the phenomenon of selectivity. He concluded that during hydrogenation of oils, the fatty acids containing two or more double bonds get saturated before oleic acid starts hydrogenating. Shortly afterwards Burchenol⁸ gave the idea of controlled selectivity, which means that the preferential saturation of double bonds can be controlled by selecting the conditions of hydrogenation. Since then a number of extensive investigations on the preparation of catalysts having desired selectivity have been reported in the literature.

H.K. Moore⁹ and associates inferred that the hydrogenation process was selective; linolein passing to olein before any appreciable amount of olein was hydrogenated into stearin.

Bailey and Fisher¹⁰ studied the relative reactivities towards hydrogenation of the di and tri-ethenoid acids in hydrogenated cottonseed, soybean and linseed oils. They recognised that hydrogenation reaction is inherently quite selective but the selectivity is never perfect.

Boelhauwer¹¹ studied the displacement of the double bonds of methyl esters of oleic, elaidic, petroselinic and linoleic acids during hydrogenation. He proved the formation of large amounts of positional isomers. Migration of the double bonds in both directions took place, but it was strongly pronounced in a direction opposite the ester group.

NATURE OF THE HYDROGENATION PROCESS.

Armstrong and Hilditch¹² studied the mechanism of hydrogenation in liquid phase. They concluded that hydrogenation under these conditions at a surface of metallic nickel is to be considered as affected by the temporary union of the unsaturated organic compound and of hydrogen with nickel, followed by a break down of this intermediate complex to yield a fatty acid radical of increased saturation plus the free nickel catalyst.

They also put forward the view of catalytic hydrogenation and dehydrogenation in the liquid state. On the basis of this theory they have explained the formation of various iso-oleic acids during the hydrogenation of unsaturated glyceride oils.

Allen and Kiess¹³ published an important finding that during the hydrogenation of octadecenoic acids, migration of the double bonds occurred equally in each direction. The positional isomers that are formed are composed of the 1:2 equilibrium mixture of cis and trans. They suggested that a partial hydrogenation and dehydrogenation theory may be applied to explain the simultaneous formation of both positional and geometrical isomers.

TYPES OF NICKEL CATALYSTS

Catalysts for the hydrogenation of fats and oils can be classified in different ways. (1) According to one classification, the terms "wet reduced" and "dry reduced" are employed depending upon whether or not reduction of a nickel salt is carried out while it is suspended in oil. (2) Catalysts are also classified as "supported type" and "unsupported type"

whether or not they are supported on an inert and refractory carrier like diatomaceous earth. (3) Then catalysts have been classified according to whether or not the catalysts are promoted¹⁴ by other suitable metals.

Manufacture of the nickel catalysts: There are three principal methods of preparing nickel in a desired dispersed and active form^{15,16}.

The first involves precipitating nickel carbonate, or nickel hydroxide from solution of either chloride, or nitrate or sulphate of nickel. Supports in the form of siliceous material like diatomaceous earth can and frequently are added during preparation of the catalyst. The resulting powder is reduced at a high temperature (370° to 540°C).

In the second method of catalyst preparation, generally termed "wet reduction"; a finely powdered nickel salt like formate is suspended in oil. It is heated to a temperature sufficient to decompose the salt under atmosphere of hydrogen which carries away volatile decomposition products. The reduction temperature is not allowed to exceed 240°C ., to avoid thermal decomposition of the oil.

The third process of catalyst preparation is the well known 'Raney method' where nickel aluminium alloy is employed. The material is commonly called "Raney nickel".

The catalyst preparation thus has become a specific problem. The precipitated type of catalyst requires great care in carrying out many operational details. Factors which influence the final product include the selection of the type

precipitant, relative quantities of reactants, solution concentrations, method of adding reactants, temperatures, washing and drying procedures, etc. The material after dry reduction, is highly pyrophoric and is suspended in oil before it gets exposed. Even with all these precautions, absolute uniformity of the product is hardly attained.

The characteristics of the wet reduced nickel catalyst are influenced by the conditions of preparation, especially the temperature at which the nickel salts are used and salt of nickel used for the preparation of catalyst.

Relation of catalyst to composition of hydrogenated fat:

A large part of the technology of hydrogenation deals with the control of hydrogenation conditions with a view to obtain the proper balance between saturated (stearic) acid and iso-oleic acids formation. The hydrogenation of oil to a low iodine value to yield hard oil or stearine is the simplest of hardening operations. There the factors of selectivity and iso-oleic acid formation are not involved. But in the preparation of different hydrogenated food products, the optimum selectivity increases in the order: ordinary shortenings, high stability shortenings (frying fats) and margarine oils. The characteristics of vanaspathi are very similar to those of margarine oils. It is relatively firm at room temperature but substantially free of glycerides which generally do not melt at the temperature of the mouth i.e. melting at about 37°C .¹⁹ In its manufacture, therefore, it is absolutely essential to avoid any considerable formation of saturated acids and to build up the required low temperature body largely through the formation of iso-oleic acids. Selective hydrogenation is equally necessary for the stability

of the product. With the same fall in iodine value, a non-selective catalyst will allow a substantial amount of linoleic acid to remain in the product resulting in its early oxidation and spoilage. Such a product will have a poor consistency at low temperature.

In practice, the quantities of saturated acids and iso-oleic acids produced at a specific iodine value or a linoleic acid content are of paramount importance because of the effect of these two acids on the consistency of the final product. Different catalysts have been found to give different amounts of iso-oleic acids at the same level of saturated acid formation and very low catalyst concentration of catalyst tend to make both saturated acids and iso-oleic acids high.

From the above facts, the necessity of finding a suitable nickel catalyst and the most favourable conditions of hydrogenation with a particular sample of the catalyst to get the desired quality of the product is a natural conclusion. Further in the course of such an investigation, it seemed desirable to compare the relative merits of different forms of nickel catalyst prepared under different conditions.

The actual procedures employed for the manufacture of catalysts have generally been kept secret. Moreover very large quantity of nickel catalyst used in India is prepared from nickel formate. Until recently, the catalysts employed for fatty oil hydrogenation were invariably manufactured by the individual oil processor for his own use. But of late years ready made imported catalysts of good quality like

'Rufert' nickel catalyst flakes" have become available and they on account of several advantages are becoming very popular. As nickel formate and several ready made catalysts have to be imported and also in view of the fact that an economic process^{17,18} has recently been developed in the National Chemical Laboratory for the recovery of nickel from the spent hydrogenation catalyst in the form of its basic carbonate, hydroxide, or sulphate, it was considered of interest to carry out the research work on utilisation of alternative cheaper salts of nickel in the preparation of the catalyst for the vanaspati industry.

The investigations carried out by the author in these directions are reported in the succeeding chapters.

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CHAPTER I.

NICKEL FORMATE FOR THE PREPARATION OF UNSUPPORTED CATALYST FOR THE HYDROGENATION OF OILS.

Nickel catalyst prepared by the pyrolytic decomposition of nickel formate using wet reduction process gives one of the most widely used material for the hardening of glyceride oils. Nickel formate is one of the simplest nickel salts available for the manufacture of nickel catalyst.

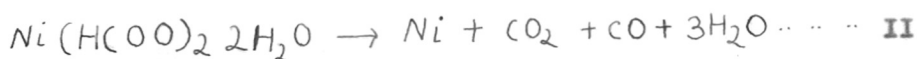
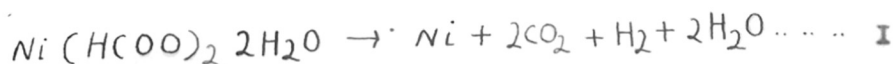
Sabatier¹ fostered hydrogenation in the vapour phase. He used nickel catalyst made by dry reduction process. Norman² put similar dry-reduced catalyst in liquid oil. He found that the activity of nickel was not destroyed although nickel was immersed in liquid medium. In fact, it was Norman² who first added hydrogen to oil and made oil hardening industry a practical proposition. But the industry was faced with innumerable difficulties in the preparation of dry-reduced catalyst on a large scale. A tremendous advance in simplicity of catalyst production and freedom from the hazards of explosion due to pyrophoric oxidation was made when the method of wet reduction was developed and introduced by Ellis³.

The wet reduction process is distinguished from dry reduction one by the fact that the catalyst is formed in oil medium. From the time of the wet reduction process has become known, nickel formate is extensively used as the raw material for preparing the catalyst. Nickel formate has got many advantages. The main advantage is the ease of preparation of the catalyst from it. The salt is simply heated in the oil to be hydrogenated thus eliminating the need

for a hazardous dry-reduction furnace. Out of other advantages, a few may be mentioned such as the activity of catalyst prepared from formate is reasonably uniform, the selectivity of such a catalyst is good, the formation of isomers during hydrogenation is not excessive and the catalyst is less affected by the presence of soap, albuminous, mucilaginous and pectic substances initially present in the oil. These impurities considerably affect the dry-reduced catalyst from nickel carbonate precipitated on diatomaceous earth but the formate produces a relatively active catalyst.

The formate catalyst has got a few disadvantages too. The main draw-back is the formation of colloidal catalyst, even when close attention is paid to the details of its preparation. Complete filtration of such a catalyst from hydrogenated oil even through the bed of diatomaceous earth is difficult. This imparts a dark colour to the finished product. Therefore, the hydrogenated oil with nickel formate catalyst always requires secondary treatment with caustic soda and bleaching clay.

The decomposition of nickel formate dihydrate on heating has been explained to occur in the following two ways¹⁴.



Water of crystallisation begins to come off at about 150°C. Decomposition of the formate itself occurs over the temperature range of 1700-2400.⁴ According to Dean⁵ the

main reaction is that given by equation I. If the temperature of the mixture is raised to 240°C too rapidly, the thermal decomposition of formate takes place according to the equation II and the catalyst produced is poisoned by carbonmonoxide.

A typical plant scale preparation of catalyst from nickel formate has been described by Wurster⁴. According to this procedure, the same oil which is to be hydrogenated is placed in a reducer admixed with nickel formate. Usually a ratio of one part of nickel salt to four parts of oil is kept. Hydrogen is introduced at 130° and the decomposition begins at 150°C . The reducer is kept vented all the time. The water of crystallisation escapes vigorously around 190°C . The oil starts to harden when the steam is driven off. The temperature rises rapidly to 240° - 250°C , when the oil smokes considerably. In order to get good activity, the charge is maintained at this temperature for half to one hour, depending upon the age of the nickel salt because it is reported that the freshly precipitated salt reduces rapidly at low temperatures.

It is claimed⁶ that the reduction of the formate is a purely thermal decomposition, independent of the added hydrogen. Dobychin⁶ has shown that the use of inert atmosphere of hydrogen in catalyst reducer gives a catalyst five times more active than the one prepared in vacuo. Further catalysts prepared from nickel formate by wet reduction process exhibit higher activity than those prepared from the dry salt. The oil medium hinders recrystallisation and sintering⁷ and produces a more dispersed catalyst.

The decomposition of nickel formate has also been studied by Balandin⁸. He has concluded that nickel catalysts obtained by decomposition of formate in oil medium are catalytically active whereas those obtained by decomposition in air or nitrogen atmosphere are almost inactive.

Colloidal nickel catalysts: Colloidal nickel catalyst from nickel formate is not considered to be highly satisfactory because it suffers from certain inherent drawbacks. They are subject to sudden coagulation and to slow decomposition. Their separation from the finished product is very difficult.

As pointed out earlier, the activity and selectivity of a nickel catalyst is much influenced by the conditions of preparation of the catalyst, especially the temperature to which it has been subjected. The surface properties of nickel reducible at different temperatures vary as indicated by its colour. Armstrong and Hilditch⁹ state that the pyrophoric character of nickel is in no way related to its catalytic activity.

There is considerable difference between the temperature at which nickel formate commences to decompose and that at which it is completed¹⁰. Similarly period of reduction is another important factor governing the activity and selectivity of nickel formate catalyst. Complete reduction of formate is not affected below 250°, but many plant operators observe that the maximum temperature of 250° mentioned by Wurster⁴ is higher than desirable.

These facts necessitated of finding suitable

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conditions for the preparation of nickel catalyst from nickel formate by wet reduction process. This chapter deals with the work carried out on the preparation of unsupported catalyst from nickel formate at various temperatures by wet reduction process together with the conditions under which formate can give most selective and active catalyst useful for hydrogenation of oils for the manufacture of vanaspati.

E_X_P_E_R_I_M_E_N_T_A_L.

PREPARATION OF NICKEL CATALYST AT VARIOUS TEMPERATURES.

The effect of reduction temperature for the preparation of catalyst from nickel formate by wet reduction process was studied by preparing five samples of catalysts at different temperatures. The process is described below.

Nickel formate (58 g.) and refined groundnut oil (232 g.) were taken in a three-necked (500 c.c.) round bottom flask equipped with a mercury sealed stirrer. A slow stream of hydrogen gas was bubbled through the oil-nickel formate mixture. The residual gases were allowed to escape from the side tube. The contents of the flask were first heated to 150°C , when the initial reaction began. The temperature was kept at about 190°C until this preliminary reaction in the reduction was over and the moisture driven off. The temperature was then raised to 232°C (450°F) to 238°C (460°F) and kept for 2 hrs., when the entire charge of the catalyst in the flask became jet black and no green particles were visible. At this stage the heat was turned off but the agitation and the introduction of hydrogen were continued during the cooling operation when the temperature came down to 100°C . The excess of oil from oil-nickel catalyst mixture was separated by filtration through double sheets of Whatman No.1. filter paper with the aid of a hot filter funnel so that the concentration of nickel in the congealed catalyst mass was about 25 per cent. The nickel content in the catalyst was determined by the method given below.

A well mixed sample of catalyst (1 g.) was digested in 40 ml. of dilute nitric acid (1:1) for a period of 10 to 15 minutes. Hot water (100 ml.) was added and the solution boiled for five minutes. The latter was filtered, washed and cooled to room temperature. To the filtrate, diluted to 400 ml., were added a saturated solution of sodium pyrophosphate (75ml.), ammonium sulphate (4 g.) and ammonium hydroxide sufficient to make it faintly alkaline. A 3% solution of potassium iodide (15 ml.) was added. The mixture was then titrated with standard potassium cyanide until cloudiness first formed just disappeared.

Similarly four other samples of catalysts were prepared at 460°-470°F, 470°-475°F, 475°-485°F and 480°-485°F.

COMPARATIVE EVALUATION OF THE NICKEL CATALYSTS.

The comparative activities of the above five nickel catalysts were tested by conducting the hydrogenation of refined groundnut oil (500 g.) in a laboratory Parr's medium pressure hydrogenation apparatus (Fig. 1) equipped with the control of temperature and pressure. The speed of agitation was maintained at 525-550 r.p.m. The amount of catalyst added was 40 gms. containing one gram of the metal equivalent to 0.2 per cent nickel on the weight of the oil. The temperature and pressure of hydrogenation were 176°-182°C and 80-90 p.s.i. (gauge). The purity of hydrogen was 99.97 per cent. Passage of hydrogen was continued till the product gave a slip point 36°-37°C¹⁵ as determined by the capillary method. At this stage, a mixture of decolourising carbon (5 g.) and hyflo-supercel (5 g.) was added and the hydrogenated oil separated by filtration through Whatman No.1.

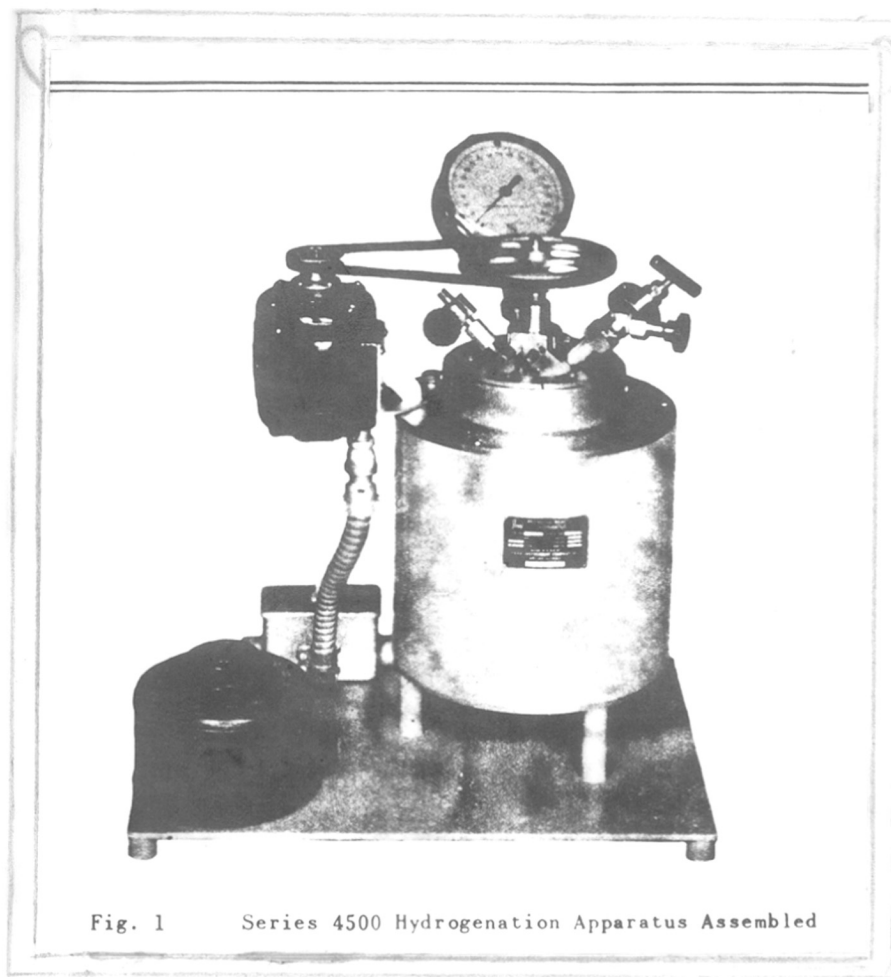


Fig. 1.

filter paper. The following characteristics were determined.

The hydrogenation time was reckoned as the period from the start of hydrogenation till a slip point 36° - 37°C ^s was attained by the fat.

The congeal point was determined by the method described by Bailey¹¹.

The consistency of the fat at 15°C was measured by the standard penetrometer IP 50/48 designed for lubricating greases.

The Butyro-refractometer readings at 40°C were also recorded.

The iodine value ($\frac{1}{2}$ hr. Wij's) of the fat and titre tests of the fatty acids were found out by A.O.C.S. Official Method cd.1-25 and CC, 12-41 respectively.

The saturated and iso-oleic acids in the total fatty acids were determined by the method of Cocks, Christian and Harding¹².

The spectroscopic method as given by Hilditch, Patel and Riley¹³ was employed for the estimation of linoleic acid.

Finally the per centage values of the above acids when subtracted from hundred gave the per centage of oleic acid.

The data from the five nickel catalysts and also by using standard 'Rufert' nickel catalyst are given in Table I. The characteristics of groundnut oil used in the experiments and similar analytical results for four well known commercial

brands of vanaspati are also included for comparison.

Observations.

The results in Table I indicate that the nickel prepared at 460°-470°F leads to the more selective hydrogenation of the oil and compares favourably with 'Rufert' catalyst in respect of congeal point, consistency, refractive index, iodine and titre values of the fat products.

It is also noticed that the selectivity and the concurrent formation of iso-oleic acids depend upon the conditions under which the catalyst is prepared. Presumably this may be due to the dissimilarities in their sub-microscopic physical texture.

Heating during the preparation of the catalyst either below 460°F or above 470°F gives a less selective catalyst.

It has been found that nickel formate without support in the manner described above forms partly a colloidal nickel catalyst. Not much satisfaction is afforded by the use of such a type of catalyst. In addition to offering negligible advantages, this colloidal catalyst has certain big draw backs. It is subject to sudden coagulation. It increases the difficulty of separating from the finished product.

The effect of aging on the reduction temperature of nickel formate

Freshly prepared nickel formate reduces readily at low temperatures if it is finely dispersed in the oil. Experiments have shown that nickel formate, which could be

reduced to selective condition at 460°-470°F. when fresh, did not do so even at 470-475°F. after storage for one year. It was observed that the formate on long storage becomes dull green in colour. To achieve good selective catalyst out of old nickel formate, it became, therefore, necessary to decompose the material at 475°-480°F so that catalyst of identical properties could be obtained. A determining factor in the temperature of reduction of nickel formate therefore appears to be its age.

The effect of heating time on the selectivity of catalyst from formate.

It has been observed that the formate salt usually takes about half an hour to reduce at 250°C which is enough to produce an active catalyst with good selectivity. The reduction of formate for less than thirty minutes produces catalyst of moderate activity and non-selectivity. Similarly continued heating of catalyst after completion of the secondary reaction when the frothing ceases results into sintering of the active metal with a fall in its activity and selectivity.

TABLE I.

Hydrogenation of refined groundnut oil with various nickel catalysts.

No. Nickel catalyst prepared at Op.	Hydrogenation time. hr. mts	Congeal point °C.	Penetration (dial reading) mm/a	Butyro-refractometer Reading 40°C.	Iodine value (Wt%)	Filter value °C	Component fatty acids			
							Saturat- ed acids %	Iso- oleic acids %	Linoleic acid %	Oleic acid %
1 450-460	1 50	24.8	305	55.60	80.6	32.6	19.4	13.2	16.5	50.9
2 460-470	1 55	32.6	35	51.70	56.6	37.2	30.2	35.5	0.2	34.1
3 470-475	1 36	15.0	400	57.20	88.1	31.2	18.3	3.6	24.3	53.8
4 475-480	1 25	14.0	380	57.50	85.8	32.2	19.7	10.9	22.5	46.9
5 480-485	1 12	12.0	soft	56.30	85.9	32.2	18.3	4.9	23.8	53.0
6 Ruffert catalyst	1 15	31.2	44	51.0	57.5	35.4	23.3	17.3	nil	54.4
7 Refined groundnut oil (unhydrogenated)	-	-	-	58.16	93.2	31.6	15.4	-	28.7	55.9
8 Commercial Brand I (Vanaspatti)	-	30.4	35	52.00	68.3	39.2	26.6	41.2	2.9	29.3
9 Commercial Brand II (Vanaspatti)	-	30.0	63	52.66	63.2	32.2	28.9	33.7	0.1	37.3
10 Commercial Brand III (Vanaspatti)	-	30.6	24	52.16	62.6	34.6	27.1	36.7	0.1	36.1
11 Commercial Brand IV (Vanaspatti)	-	30.6	35	52.50	63.7	33.8	31.4	37.9	3.0	27.7

R_E_F_E_R_E_N_C_E_S.

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CHAPTER II.

CONDITIONS OF HYDROGENATION OF OILS.

Besides the quality of the catalyst, its quantity and various conditions such as temperature, pressure and time of hydrogenation influences a great deal on the final product that is obtained.

Dhingra, Hilditch and Rhead¹ studied the influence of catalyst concentration on the hydrogenation of cotton seed oil. They found that the proportion of iso-oleic acids produced depends mainly on the temperature of hydrogenation and to some extent on the catalyst concentration. It increases with rise of temperature and also with increasing concentration of catalyst at a given temperature.

Bailey, Feuge and Smith² studied the effects of the factors governing the hydrogenation of cottonseed and peanut oils, like temperature, catalyst concentration, hydrogen pressure, degree of agitation and nature of the catalyst. They inferred that the rise in temperature increases the selectivity of the reaction and at the same time increases the formation of iso-oleic acids. Decrease of hydrogenation pressure increases selectivity using the same conditions, increase of catalyst concentration increases selectivity. It has also been shown that selectivity is increased by less vigorous agitation and vice versa when other conditions are constant.

Feuge and co-workers³ found that the rate of formation of trans isomers in methyl oleate undergoing hydrogenation is increased by increasing the temperature and catalyst

concentration and by decreasing the degree of dispersion of hydrogen.

Sims⁴ concluded from his investigations on the variations in the chemical and physical properties of soybean oil hydrogenated under widely varying conditions that at moderate pressures selectivity was found to vary directly with catalyst concentration and inversely with agitation speed. However at high pressures the effect of these variables was reversed. The selectivity varied directly with the amount of agitation and inversely with the catalyst concentration.

Sims and Hilfman⁵ from their experiments on the formation of trans isomers during the hydrogenation of glyceride oils inferred that the conditions which favoured the selective hydrogenation of glyceride oils also favoured the development of trans isomers.

In series of papers published by Allen and Kiess⁶ in 1956, the authors showed the formation of various types of isomers during hydrogenation of esters of 9:12-linoleic acid, 10:12-linoleic acid and β -elaeostearic acid.

Most of the work tend to prove that the course of the catalytic hydrogenation of the ethylenic linkages in oil depends upon a number of factors. The relative reactivity of a given ethylenic linkage is affected not only by its position with reference to an acyl group and its proximity to other ethylenic linkages in the same group but also by the amount and type of catalyst and other operating conditions. Very frequently a given linkage does not undergo a straight forward reduction, but rather the first reaction is a shift to a new position or its re-arrangement to another

geometric form. Both of these changes may also take place before the double bond is hydrogenated.

Operating variables during hydrogenation: While hydrogenation tends to be naturally selective, the plant operator has four variables under his immediate control which he can manipulate to change the selectivity to a marked extent. The variables are temperature, type and concentration of catalyst, hydrogen pressure and agitation. These variables exert their influences in a complex manner on the composition of the final product obtained on hydrogenation.

Present work:

With a view to elucidating the course of the hydrogenation reaction and the effect of the various conditions on the composition of hydrogenated product, the reactions occurring under varying conditions were studied. The previous chapter dealt with the work carried out on the preparation of suitable unsupported catalyst from nickel formate by wet reduction process. As a result of this work, the catalyst prepared at 460°-470°F under the conditions mentioned was found as the most efficient. The present chapter summarises the work carried out for finding the conditions under which hydrogenated product satisfying the maximum requirements of vanaspati can be obtained by using such a catalyst.

E_X_P_E_R_I_M_E_N_T_A_L.

(A) EFFECT OF CATALYST CONCENTRATION ON HYDROGENATION OF GROUNDNUT OIL:

Bailey² found that increase of the catalyst concentration has the effect of simultaneously making the hydrogenation more selective and causing more iso-oleic acids to be formed, whereas slowing hydrogenation by reducing the catalyst concentration makes it non-selective. In order to find out the most suitable concentration of the catalyst, hydrogenation of batches of 500 g. of refined groundnut oil were conducted in presence of nickel catalyst prepared at 460°-470°F, in quantities to get 0.05, 0.1, 0.15, 0.2, 0.25, and 0.3 per cent metal on the weight of oil in the equipment described in the previous chapter. The temperature and pressure were kept at 176°-182°C and 85-90 p.s.i. (guage) respectively. Hyflo-supercel equivalent to twice the weight of nickel was always used. The various characteristics of the products so obtained are given in Table II.

From these results, it may be seen that 0.2 per cent nickel concentration on the weight of oil gives maximum selectivity and consistency to the product. The drop in iodine value has also been the greatest at this amount of the catalyst.

(B) EFFECT OF TEMPERATURE ON HYDROGENATION OF GROUNDNUT OIL:

For oils there usually exists a well defined range of temperature within which hydrogen is effectively added. Somewhere in this interval lies the mean effective temperature, that is the temperature of maximum saturation

velocity. For a number of fatty oils, this approximates 180°C or 356°F , using nickel as catalyst.

Maxted⁷ has found that the temperature of maximum activity of nickel catalyst for the hydrogenation of glyceride oils appears to be about 175°C .

Bailey² concluded that the formation of stearic acid was repressed and the formation of iso-oleic acids simultaneously favoured by increasing the temperature.

For finding the effect of temperature on the course of hydrogenation of groundnut oil, experiments, using 0.2 per cent nickel concentration (catalyst prepared at $460^{\circ}\text{--}470^{\circ}\text{F}$) on the weight of oil at 85-90 p.s.i. and temperatures varying from 150° to 215°C were carried out. The characteristics of the various hydrogenated products thus obtained are recorded in Table III.

The results indicate that upto a certain increase in temperature of hydrogenation (182°C), the selectivity and the consistency of the product increases and a regular drop in iodine value is obtained. The time of hydrogenation at lower temperatures upto 166°C has been much more than in the range of $176^{\circ}\text{--}182^{\circ}\text{C}$. At higher temperatures from 188°C onwards, the selectivity decreases and the product obtained is softer. The fall in iodine value also is less. On the whole, the hydrogenation temperature in the range of $176^{\circ}\text{--}182^{\circ}\text{C}$ gives a product of maximum consistency and drop in iodine value.

(C) EFFECT OF PRESSURE ON HYDROGENATION OF GROUNDNUT OIL:

The majority of hydrogenation reactions usually proceed at atmospheric pressure. But sometimes there is convenience in working at higher pressures. The direction of the hydrogenation reaction may be controlled by increasing the pressure and the time of hydrogenation for reaching to the same consistency of the product may be lessened.

Armstrong and Hilditch⁸ studied the influence of variation in the hydrogen pressure. They found that the velocity of hydrogenation is directly proportional to the hydrogen pressure in the absence of other disturbing factors.

Bailey and co-workers² studied the influence of pressure on the fatty acid composition of hydrogenated oils. They concluded that within the range of pressure of ordinary commercial hydrogenation, i.e., about 1 to 6 atmospheres or upto about 75 lbs. pressure, the hydrogenation rate is approximately proportional to the absolute pressure. They further found that an increase in pressure decreased the selectivity and also inhibited iso-oleic acid formation.

For finding the effect of pressure on the time of hydrogenation and the product obtained, experiments were conducted at pressures varying from 5 to 100 p.s.i. with charges of 500 g. of refined groundnut oil, using 0.2 per cent nickel at 176°-182°. The catalyst prepared at 460°-470°F was used. Two grams of hyflo-supercel were also added in each experiment. Hydrogenation was stopped when the product attained a capillary slip point 36°-37°C. The results are given in Table IV.

The results indicate that at very low pressure of the order of 5-10 p.s.i., a hydrogenated product of fair selectivity and good consistency is obtained but the time required to attain the desired slip point is abnormally high. The selectivity in hydrogenation and consistency of the product decrease and also the iodine value increases upto a certain maximum pressure of 70 p.s.i. In the range of 75-90 p.s.i., the hydrogenation becomes quite selective and products of good consistency and iodine values are obtained. These characteristics are still enhanced on increasing the pressures upto 95-100 p.s.i. but the product becomes harder than is usually required in the industry. On the whole a pressure of 75-90 p.s.i. is found to be quite satisfactory for obtaining the desired product under the conditions employed.

HYDROGENATION OF VARIOUS OILS.

As groundnut, cottonseed, linseed and mustard oils are major indigenous produce of India and the Planning Commission has also stressed upon the desirability of the utilization of cottonseed oil in vanaspati industry, these four oils were hydrogenated using 0.2 per cent nickel on the weight of oil. The catalyst prepared at 460°-470°F was employed. The temperature and pressure of hydrogenation were maintained at 176°-182° and 75-90 p.s.i. In the case of groundnut and cottonseed oils, 75 per cent of the used catalyst was mixed with 25 per cent of the fresh material and the hydrogenation of another batch of the same oil was again undertaken. Such experiments were repeated four times with the above two oils. The hydrogenation was considered as

complete when the product attained a capillary slip point 36° - 37°C . The hydrogenation of mustard oil to the required extent was not found possible. It was however found that if after conducting the hydrogenation for about one hour, the poisoned catalyst was replaced by the fresh catalyst, the hydrogenation proceeded smoothly to completion.

The characteristics of the various oils and those of their hydrogenated products obtained as above are given in Table V.

DISCUSSION:

The work mentioned above has been carried out in a laboratory hydrogenation apparatus. Since there are differences in the efficiency of agitation of hydrogen dispersion between laboratory and commercial hydrogenators and also among different models of commercial apparatus, results at a given temperature, pressure and catalyst concentration generally vary from one hydrogenator to another. Nevertheless the work reported gives a clear idea of the most suitable conditions for hydrogenation in the same apparatus. As testing of other catalysts prepared from different nickel salts, supports and promoters described in the next chapters has been carried out in the same equipment, the study forms a basis of evaluation of the different nickel catalysts for the hydrogenation of oils.

Bailey², et al have reported that increasing the concentration of a given catalyst with other factors constant, has the effect of making the reaction more selective and increase the concentration of oleic acids. The results given in Table II, however, show that selectivity in hydrogenation

increases upto a certain concentration of the catalyst (0.20%) after which it almost remains unchanged.

It has also been mentioned² that selectivity is enhanced by increasing the temperature of hydrogenation and formation of iso-oleic acids also increases at higher temperatures. This has been found to be the case upto the maximum hydrogenation temperature of 182° (Table III). Above this temperature the hydrogenation becomes non-selective as evidenced by the increased quantities of linoleic acid. As has been held by various investigators⁹ this may be due to the dehydrogenation also accompanying the hydrogenation of the fat under these ranges of temperatures. Less formation of saturated acids, smaller drop in iodine values and formation of softer products at hydrogenation temperatures 188°-207°C is a clear indication that appreciable amount of dehydrogenation is taking place under these conditions. The hydrogenation appears to be much accelerated at temperatures of the order 210°-215°C.

It has further been reported that increasing² the hydrogenation pressure decreases the selectivity and also inhibits iso-oleic acid formation. This has actually been found the case (Table IV) upto the pressure of 65-70 p.s.i. while at low pressures of 5-30 p.s.i. the hydrogenation was quite selective and consequently more of iso-oleic acid formation. At higher pressures selectivity again increases. But the time required for hydrogenation under low pressures (10 p.s.i.) is much more than that at higher pressures of the order 75-90 p.s.i. Hence in all the experiments a

pressure of 85-90 p.s.i. for hydrogenation has been employed.

The results of hydrogenation of four vegetable oils given in Table V lead to some interesting conclusions. As is well-known, the re-usage of the catalyst decreases the selectivity to some extent in the case of groundnut oil. But in the case of cottonseed oil the selectivity has been found to progressively increase to some extent in the four charges tried. The consistency of the different batches, however, differs within wide limits. For the sake of getting a uniform product, it will, therefore, be preferable if the three or four batches, hydrogenated with used catalyst may be mixed together before packing for sale.

After a definite number of charges of hydrogenations with such a catalyst, it will be preferable if it is entirely replaced by the fresh catalyst for subsequent hydrogenations.

It is not desirable both for the sake of economy and the quality of the product to take a very unsaturated type of oil for hydrogenation. The results of linseed oil show that hydrogenation of the oil takes a very long time and even then a product of less consistency is obtained.

The catalyst evidently is poisoned when hydrogenation of mustard oil which contains a sulphur compound in it is undertaken. As is well-known, the hydrogenation of the oil is possible if the catalyst is added in two instalments. The first part of the nickel removes the sulphur constituent from the oil and the hydrogenation proceeds smoothly when a fresh catalyst to

such a treated oil is added. The iso-oleic acids contents in this case has been exceptionally high. This may be due to the reason that a part of erucic acid also comes along with the insoluble lead salts in the separation of fatty acids by this method^{10.11}.

Conclusions:

1. A hydrogenation temperature 176-182°C and pressure 85-90 p.s.i. with nickel concentration 0.2 per cent on the weight of the oil has been found to give a product of maximum selectivity and desired consistency.

2. A highly unsaturated oil may not give a product of desired consistency.

3. The hydrogenation of oils containing materials which poisons the catalyst such as mustard oil is better accomplished if a part of the catalyst is added first, removing it after sometime and adding the fresh catalyst again.

4. The reusage of the spent catalyst may be limited to 3 or 4 batches of the oil. Even these batches may be mixed together in order to get uniform product.

*

TABLE II.

Effect of concentration of nickel on the hydrogenation of groundnut oil.

No.	Nickel on oil weight %	Hydrogenation time hr.	mts.	Congeal point °C	Penetration (Dial reading) mm/10	Butyro-refractometer reading 40°C.	Iodine value (Wtgs)	Titer value	Component fatty acids.			
									Saturated acids %	Iso-oleic acids %	Linoleic acid %	Oleic acid %
1	0.05	2	30	29.8	52	51.5	60.5	34.7	28.6	31.7	1.3	38.4
2	0.10	2	5	31.0	45	51.3	58.6	35.2	27.4	29.7	1.1	41.8
3	0.15	2	0	30.4	92	52.0	63.2	34.6	26.9	25.3	0.5	47.3
4	0.20	1	55	32.6	35	51.0	56.6	37.2	30.2	35.5	0.1	34.2
5	0.25	1	55	30.0	87	51.5	60.4	34.4	23.9	24.5	0.3	51.3
6	0.30	1	50	29.8	55	51.5	61.2	34.9	28.5	32.1	0.2	39.2

TABLE III.

Effect of temperature on the hydrogenation of groundnut oil.

No.	Temperature of hydrogenation °C	Hydrogenation time hr. mts.	Congeal point °C	Penetration (dial reading) mm/10	Butyro-refractometer reading 40°C.	Iodine value (Wtgs)	Titer value °C	Component fatty acids		
								Saturated acids %	Iso-oleic acid %	Oleic acid %
1	150-155	4 33	26.6	59	51.5	60.6	35.2	28.5	28.2	0.5
2	160-166	4 22	31.2	47	51.3	57.8	38.3	28.7	25.9	0.6
3	176-182	1 55	32.6	35	51.0	56.6	37.2	30.2	35.5	0.1
4	183-188	1 55	28.6	112	52.5	64.6	34.3	26.6	24.6	3.4
5	193-199	1 55	26.8	100	52.5	63.7	34.8	26.3	26.6	3.1
6	201-207	1 40	27.0	75	52.2	62.8	35.0	27.1	36.6	1.3
7	210-215	1 20	27.8	38	51.5	60.4	35.4	28.0	30.8	1.7

TABLE IV.

Effect of pressure on the hydrogenation of groundnut oil.

No.	Pressure of hydrogenation p.s.i.	Hydrogenation time hr.mts.	Congeal point °C	Penetration (dial reading) mm/10.	Butyro-refractometer reading 40°C.	Iodine value (Wtgs)	Filter value °C.	Component fatty acids		
								Saturated acids %	Iso-oleic acid %	Linoleic acid %
1	5-10	8 20	29.4	35	51.34	61.5	35.2	28.3	40.9	0.3
2	10-15	8 17	28.6	63	52.16	63.3	34.2	25.9	30.7	0.5
3	25-30	5 40	27.1	62	52.50	64.1	34.1	26.4	35.9	0.5
4	35-40	3 50	26.6	67	52.84	64.5	33.6	24.7	26.1	0.7
5	45-50	3 0	27.1	82	53.00	64.4	32.8	33.9	33.6	1.2
6	55-60	3 0	26.2	98	53.16	64.6	32.6	23.4	27.3	2.2
7	65-70	2 45	26.6	104	53.66	70.8	30.6	23.6	25.5	3.6
8	75-90	1 55	32.0	41	51.34	60.3	35.8	27.5	37.8	0.5
9	85-90	1 55	32.6	35	51.00	56.6	37.2	30.2	35.5	0.1
10	95-100	2 5	33.8	24	50.84	56.9	39.7	31.4	37.8	nil

Hydrogenation of four vegetable oils.

Oil or hydrogenated product	Hydrogenation time hr. mts.	Congeal point °C.	Penetration (dal reading) mm/10	Butyro refracto-meter reading 40°C	Iodine value (Wt.%)	Titer value OC	Component fatty acids.			
							Saturated acids %	Iso- oleic acids %	Linoleic acids %	Oleic acid %
Refined groundnut oil	- -	- -	- -	58.16	92.4	31.4	15.8	- -	26.9	57.3
(unhydrogenated)	2 10	30.4	34	51.00	57.9	35.7	25.8	37.8	0.1	36.3
Hydrogenated product I	2 10	26.6	67	52.00	62.0	34.4	27.8	33.7	2.0	36.5
" II	1 55	26.5	66	51.84	61.8	34.6	29.7	33.6	1.8	34.9
" III	1 50	26.1	65	51.76	61.6	34.8	30.0	36.5	1.9	31.6
Refined cottonseed oil	- -	- -	- -	60.5	104.6	34.1	14.8	- -	52.8	32.4
(unhydrogenated) p	2 45	27.8	30	52.84	66.8	35.0	19.6	43.2	8.3	28.9
Hydrogenated product I	3 0	28.2	54	53.34	66.6	35.4	19.7	30.6	7.9	31.8
" II	2 45	28.4	51	53.34	65.2	34.6	20.7	44.7	4.6	30.1
" III	2 40	28.6	48	52.5	63.7	35.4	20.6	46.5	2.1	30.3
Refined linseed oil	- -	- -	- -	74.5	188.9	21.0	8.9	- -	23.9	17.0
(unhydrogenated)	4 20	29.6	92	59.0	74.17	43.3	25.0	40.4	0.9	33.7
Hydrogenated product	- -	- -	- -	62.32	96.0	17.5	11.7	- -	10.4	29.3
Refined mustard oil	2 30	29.8	43	54.85	67.6	30.8	25.9	64.4*	0.2	9.5
Hydrogenated product	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
* also contained erucic and iso-erucic acid.										

Erucic acid
46.5

: R_E_F_E_R_E_N_C_E_S:

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CHAPTER III.

SUPPORTS FOR THE NICKEL CATALYST.

A comparative study of the activity of various samples of nickel catalysts prepared from nickel formate by wet reduction process at different temperatures ranging from 450° to 480° F for the hydrogenation of refined groundnut oil has already been summarised. The present chapter deals with the investigations to find out the most satisfactory carrier for the nickel catalyst. In general, by the term "carrier" is meant an inert material which acts as a base or support for the catalyst but which by itself has little catalytic activity.

Kayser¹ first introduced the use of Kieselghr as a carrier for a nickel catalyst in oil hardening industry in the United States in 1908. Later, Erdmann and Bedford² used pumice as a carrier for a nickel catalyst in the hydrogenation of fatty acids and their esters. In 1910 Paal³ used palladium on Kieselguhr in oil hardening. From that time onwards many other carriers in catalytic hydrogenation have been mentioned in literature. At present commercial catalysts do not consist of a single component. They are generally mixtures of active nickel and a base like kieselguhr. Berkman, Morrel and Egloff⁴ have reviewed the subject of carriers in detail. Work of this type carried out in recent years (1942-1952) has been summarised by Emmet⁵.

Function of a carrier:

The mechanical function of a carrier is to act as a base material for the catalyst. It serves to reduce shrinkage

of the active lattices of the catalyst. A carrier gives physical strength to the catalytic component. They are a few important effects of a carrier.

A carrier may be useful in providing a larger contact surface and at the same time a more equal distribution of the catalyst. It also prevents recrystallisation or caking together and thus preserves the fine dispersion of the catalyst. It is valuable because it hinders aggregation which otherwise may occur. Moreover a carrier may influence indirectly the activity of a catalyst by protecting it from poisons. These objectives are generally attained by the use of inert materials such as carbon, silica, zeolites, asbestos, pumice, fuller's earth, kieselguhr and other siliceous earths and clays⁴.

Incorporation of catalyst with carrier:

A catalyst may be incorporated with a carrier in a number of different ways. Each method depends upon the nature of the carrier and the type of catalyst to be supported. Three methods generally in use for this purpose are summarised below and their relative merits are also discussed.

1st Method: The method of impregnation is most common. It involves mixing a solution of nickel salt like nitrate, chloride, formate, etc. with the carrier. The resultant mixture is heated while continuously stirred. The water is evaporated which gives a solid material containing the nickel salt impregnated on the external surface of the carrier. The cake is then dried, powdered and reduced to give a catalyst supported on a carrier.

But simple impregnation may not result in a uniform catalyst distribution.

2nd Method: The method of precipitation consists in eliminating migration of the catalyst component on drying. It involves the introduction of a catalyst to a carrier as a solution or colloidal dispersion which is then precipitated so that it deposits on the carrier surface. Finally it is washed, dried and reduced.

3rd Method: Simple mechanical mixing of the catalytic component with the carrier both in the solid form is also employed. But such a procedure does not give a high degree of dispersion of catalytic material, yet the method is quite useful for many practical purposes.

Properties of carriers:

Knowledge of the nature and properties of carriers is necessary in their selection as supports for catalysts. The carriers have their structural characteristics like amorphous, or crystalline, porous, or compact surfaces. In addition to their structural characteristics, the following properties are considered in the selection of a carrier⁴.

1. Chemical composition and state of dispersion.
2. Physical properties of the surface, (porosity, adsorption, contact property, electrical properties, mechanical strength, etc.)
3. Amount and concentration of both catalyst and carrier, thickness of the catalyst layer deposited on the carrier, saturation capacity of carriers.

4. Active area of the carrier and the ratio of the catalyst atoms to the carrier atoms corresponding to the catalyzing action of the carrier-catalyst.

In using a carrier as a support for nickel catalyst for hydrogenation of glyceride oils, it is therefore important to determine (1) the type of carrier, ^{and} (2) the concentration of carrier in supported catalyst.

The depth to which the carrier particles can be penetrated by nickel is also strongly reflected in the activating ability and selectivity of the catalyst⁴.

In preparing a supported nickel catalyst, it is therefore, important to evaluate the process of depositing nickel on a carrier which will enable nickel to exhibit its maximum activity and selectivity.

A variety of materials are employed as supports for nickel catalyst used in hydrogenation of glyceride oils. Some of these materials, in addition to their function as supports, have in certain reactions a distinct promoter action. Others such as carbon, kieselguhr, and fuller's earth are useful as clarifying agents. However, there is very little information available in literature regarding the specific effects of each of these carriers on the selectivity of nickel catalyst. The work carried out in these directions is reported in this chapter.

Present work:

For studying the activity and also selectivity of the nickel catalyst on various carriers, decolourising carbon (Merck), hyflo-supercel (I.C.I.), silica gel (B.D.H.),

two samples of kieselguhr (Merck, Hopkins & Williams), fuller's earth (B.D.H.) were employed in the preparation of the catalyst from nickel formate by wet reduction process. Since it is also mentioned that excessive amount of the carrier reduces the exposed surface of the catalyst⁶, such amounts of the above materials were taken as to give a ratio of two parts of nickel to one part of the support for their comparative evaluation. The procedure for the preparation of supported nickel catalyst using the above materials has been the same in all cases and is very similar to that employed for unsupported nickel catalyst (Chapter I). For the sake of clarification, the method employed in the case of carbon is given below.

E_X_P_E_R_I_M_E_N_T_A_L.

Nickel formate (58 g.) was intimately mixed with decolourising carbon (Merck) by grinding together in a pestle and mortar. The carbon-formate mixture and refined groundnut oil (232 g.) were taken in a three-necked (500 c.c.) round bottomed flask, equipped with a mercury sealed stirrer. The mixture was slowly heated to 150°C . while bubbling a slow stream of hydrogen through it and kept vigorously stirred throughout. The exit gases were allowed to escape outside. After the initial reaction started, the temperature was raised to 190°C when most of the preliminary activity in the reduction was complete and moisture driven off. The temperature was then raised to 255°C - 260°C ^{and kept} for about 30 mins. when the catalyst became jet black in colour. This slightly higher temperature than that employed earlier in case of formate alone (Chapter I) was found necessary for complete conversion of the formate into colloidal nickel. Heating for a longer period more than 30 mins. at the above temperature (255°C - 260°C) leads to the production of catalyst of less selectivity. The material was then slowly cooled in the atmosphere of hydrogen when a jet black solid mass was obtained. The excess of oil was removed by filtration so that the concentration of nickel catalyst in the mass was very near to 25 per cent. The comparative activities of the supported nickel catalysts were tested as before by conducting the hydrogenation of refined groundnut oil (500 g.) in Parr's medium pressure hydrogenation apparatus. The speed of agitation was maintained at 525-550 r.p.m. catalyst equivalent to 0.2 per cent nickel on the weight of the oil was used in each case. Hyflo-supercel (2 g.) was also added as a filter

aid. The temperature and pressure of hydrogenation were 176° - 182°C and 75-90 p.s.i. The hydrogenation was continued till a slip point of 36° - 37°C was attained by the fat. After the addition of decolourising carbon and hyflo-supercel (5 g. each), the clear product was recovered by filtration. The characteristics of the products obtained by using nickel catalyst supported on various carriers are given in Table VI. Similar data in the case of refined cotton seed oil are recorded in Table VII.

Observations:

From the data in tables VI and VII, the following conclusions may be arrived at.

1. Nickel catalyst when supported on a carrier in the proportion of 2:1 increases the rate of hydrogenation of the oil.

2. A neutral support such as carbon, hyflo-supercel or silica gel is superior to carrier, acidic in nature, of the type of fuller's earth or kieselguhr, both as regards consistency of the hydrogenated product and selectivity of hydrogenation.

3. Out of the neutral carriers tried, hyflo-supercel is to some extent better than the others as by its use, a product having consistency very similar to that desired by the vanaspati industry is obtained. The material is also available in a uniform quality at an economic rate.

The effect of concentration of carrier on the catalytic activity of nickel

The role of carrier in the activity and selectivity of nickel is not very clear. It is true that some of the

carriers for the hydrogenating metal act to stabilize the catalyst surface. They sometimes act as promoters also to enhance the catalytic activity of nickel. But very little is known in the literature as to how the selectivity of the hydrogenating metal is affected as the content of support is changed. It is quite evident that for each combination of hydrogenating metal and Support⁷, there exists an optimum ratio of metal to carrier which will produce a maximum selectivity in the catalyst.

To find out the most satisfactory concentration of the carrier, catalysts were prepared by using hyflo-supercel so as to get a ratio to nickel 1:2, 1:1, and 3:2. Supported catalysts were also prepared by using decolourising carbon (Merck) employing 1:2 and 1:1 parts with nickel. Solid nickel formate was ground with the carrier and wet reduction using groundnut oil was done in each case. The results obtained on the hydrogenation of groundnut oil with the above catalyst using 0.2 per cent nickel on the weight of oil hydrogenated are given in Table VIII.

The results clearly indicate that concentration of carrier in proportion of one part to two parts of nickel is better than in higher amounts particularly as regards selectivity in hydrogenation, consistency of the product and to some extent in the time of hydrogenation.

Since impregnation is one of the methods⁵ for the incorporation of catalyst with carrier, a catalyst was also prepared by adding hyflo-supercel (1 part) to a hot aqueous solution of nickel formate, evaporating the water at

105°-110°C with constant stirring and finally drying it to a powder at 110°-120°C. The material was then reduced in groundnut oil. The catalyst thus obtained was used for the hydrogenation of groundnut oil. The data obtained with this catalyst are also summarised in Table VIII.

The catalyst prepared by the impregnation method gives a product of softer consistency than the one prepared by dry grinding method. As pointed by Emmet⁵ these drawbacks in the hydrogenated product may be caused by the non-uniform catalyst distribution and formation of relatively large crystals of nickel nearer or on the external surface due to migration of nickel solution from the interior pores to the external surface where liquid deposits crystals after evaporation.

Effect of concentration of supported nickel catalyst on the hydrogenation of groundnut oil.

The selectivity of hydrogenation and the concurrent formation of iso-oleic acids are favoured by a greater catalyst concentration. The most suitable amount of nickel when the unsupported catalyst is employed has already been determined. Now in order to find out a similar catalyst concentration for hydrogenation, when the supported catalyst is employed, experiments of batches of 500 g. of groundnut oil were carried out using nickel supported on hyflo-supercel in quantities to get 0.1, 0.15 and 0.2 per cent of metal on the weight of the oil. The conditions of hydrogenation were the same as maintained in previous experiments. The results are summarised in Table IX.

The values obtained show that as with unsupported catalyst, 0.2 per cent nickel concentration gives a product

of maximum selectivity and consistency and also requires least time in hydrogenation.

Conclusions:

A nickel catalyst supported on limited amounts of neutral carriers of the type of hyflo-supercel or decolourising carbon is preferable for increasing the rate of hydrogenation., to the unsupported one.

Supported nickel formate reduces at a slightly higher temperature (5° to 10°C) than the unsupported one. But additional advantage in using a support lies in the fact that the catalyst may be subjected to more severe heating in the reduction process without destroying its activity.

There exists an optimum concentration of support in the catalyst above which the supporting material has got an adverse effect on the selectivity of the catalyst. Use of nickel metal admixed with an excessive inert material such as hyflo-supercel or carbon has not given satisfactory results probably for the reason that⁶ only a small part of the film of the catalyst metal comes into actual contact with the oil to be hydrogenated and the gas. On the basis of this assumption more and more surface of the catalytic material gets coated with the supporting material as its concentration in the catalyst increases thus making the catalyst less and less effective.

TABLE VI.

Hydrogenation of refined groundnut oil in presence of supported nickel catalysts.

Amount of carrier - one part to two parts of nickel.

Oil or product hydrogenated using nickel carrier	Acidity or basicity of the carrier	Hydrogenation time hrs.min	Congeal point °C	Penetration (dial reading) mm.10	Butyro-refracto- meter reading 40°C	Iodine value (Wt.%)	Iodine value CC	Component fatty acids %		
								Saturated acids	Iso- oleic acids	Linoleic acid
Refined oil (unhydrogenated)	--	--	--	--	58.16	92.4	31.4	15.8	--	26.9
No carrier	--	2	10	34	51.00	57.9	35.7	25.8	37.8	0.1
Decolourising carbon (Merck)	neutral	1	40	25	51.00	60.6	38.4	29.5	36.0	nil
Hyflo-supercel (I.C.I.)	"	1	30	34	51.30	62.5	36.2	27.7	33.1	nil
Silica gel (B.D.H.)	"	1	35	24.0	51.10	62.3	37.0	26.4	31.6	nil
Fuller's earth (B.D.H.)	acidic 0.007% HCl	1	35	34.0	51.3	62.4	36.8	27.2	29.2	nil
Kieselguhr (Merck)	acidic 0.014% HCl	1	30	154	54.0	74.3	33.6	23.1	15.4	8.9
Kieselguhr (Hopkins & Williams)	acidic 0.025% HCl	1	40	140	55.6	74.9	33.7	19.8	10.8	8.6
										61.5

TABLE VIII.

Effect of concentration of carrier in supported nickel catalyst on the hydrogenation of groundnut oil.

Carrier	Ratio of carrier: nickel	Hydrogenation time hrs.	Congeal point °C.	Penetration (dial reading) mm/10	Butyro-refracto- meter reading 40°C.	Iodine value (Wils)	Titer value °C	Component fatty acids %		
								Saturated acids	Iso- oleic acids	Oleic acid.
Hyflo-supercel	1:2	1 30	31.2	34	51.7	62.5	36.2	27.7	33.1	nil
"	1:1	1 30	31.8	29	52.5	60.6	36.6	28.1	43.6	1.5
"	3:2	1 37	28.2	60	52.8	63.3	35.4	22.2	22.1	3.2
Decolourising carbon	1:2	1 40	33.0	24	51.0	60.6	38.4	29.5	36.0	nil
"	1:1	1 54	29.8	51	52.3	62.5	35.6	26.8	32.9	3.0
Hyflo-supercel (impregnation method)	1:2	1 20	27.6	65	52.8	63.0	35.6	26.7	19.7	1.0
										52.6

TABLE IX

Effect of concentration of nickel on the hydrogenation of groundnut oil using catalyst supported on hyflosupercel (1:2)

Nickel on oil weight %	Hydrogena- tion time hrs. mts.	Congeal point °C	Penetration (dial read- ing) mm/10.	Butyro- refracto- meter reading 40°C	Iodine value (Wijs)	Titer value	Component fatty acids %			
							Saturated acids	Iso-oleic acids	Linoleic acid	Oleic acid.
0.10	3 30	28.0	106	52.2	63.6	35.8	27.3	44.8	0.7	27.4
0.15	2 25	30.2	54	51.3	62.0	37.3	28.9	48.0	0.7	22.4
0.20	1 30	32.6	35	51.7	56.6	38.6	30.2	35.5	0.2	34.1

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VARIOUS SALTS OF NICKEL FOR THE CATALYST PREPARATION.

The preparation and activation of unsupported as well as supported nickel catalysts from the inorganic salts of nickel have been studied by many investigators.

A German patent issued to Senderens is probably the first patent recorded. The conditions of reducing nickel oxide, as far as temperature is concerned were first laid down by Sabatier and Senderens¹. Kelber² investigated the effect of reduction temperature and oxygen on the activity of nickel catalysts prepared from the basic nickel carbonate. He³ also showed that nickel oxide reduced at 450°C had very little activity while reduction at 300°C gave a moderately active catalyst. Lietz⁴ studied the preparation of nickel catalysts by reducing the basic carbonate prepared by mixing aqueous solutions of nickel sulphate and sodium carbonate. Kusama and Uno⁵ compared the activities of nickel catalysts prepared from nickel chloride and nickel nitrate. Waterman and Tussenbroek⁶ prepared a kieselguhr supported nickel catalyst by precipitating the oxide from nickel sulphate on the support. They investigated the effect of heat treatment on the activity of the catalyst. Armstrong and Hilditch⁷ found that nickel hydroxide precipitated on kieselguhr gave a very active catalyst by reduction at 500°C, while the unsupported catalyst had very little activity when reduced at this temperature. But it has a fair activity on reduction at 300°C. Thomas⁸ similarly described the reduction of nickel hydroxide with hydrogen. Maximum activity was obtained at about 300°C in the case of an unsupported catalyst and between 350°C and 500°C

with nickel supported on kieselguhr. The Hydrogenation Patent Application Society⁹ described a process of preparing nickel catalyst from nickel carbonate by heating it under a layer of oil and reducing gases under pressure. The reduction of nickel carbonate took place between 200°-250°C.

Nickel catalyst has been made similarly by various investigators¹⁰ by reduction of nickel carbonate at 90-150 atmospheres of hydrogen pressure. Ellis¹¹ has mentioned that metallic catalysts may be prepared at low temperatures by the combined use of a catalyst and high pressure. Finely divided metals have been obtained by reducing an oxide, hydroxide or salt with hydrogen in presence of a carrier at a low temperature. Kahlenberg and Ritter¹² reduced nickel chloride with hydrogen at 180°-250°C. It is stated that catalyst obtained was very good for hydrogenation of oils.

Most of the familiar nickel compounds have been investigated at one time or another as catalyst raw materials. The three most commonly known inorganic salts of nickel, the sulphate, chloride and nitrate are most useful in supplying nickel ion. Nickel oxide, hydroxide, basic carbonate and formate served as raw materials for the reduction to finely divided active nickel in the final step of catalyst preparation.

Nickel sulphate is used in very large quantities because it normally the cheapest and most commonly available salt. The normal procedure for preparing the catalyst is to precipitate nickel hydroxide or basic carbonate from solutions of this salt, often along with a carrier. The precipitate after washing, drying and grinding, is reduced with hydrogen¹³. This type of product is characteristic of the so-called

precipitated dry-reduced nickel catalyst, which is to some extent used for the hydrogenation of organic compounds.

The production of nickel catalysts by this method requires attention to many variables. Important steps are the selection of the precipitant, chemical ratio of reactants, solution concentrations, temperatures, method of mixing, washing procedure, and conditions of drying the precipitate. The basic objective throughout these steps prior to the reduction is to obtain a pure precipitate compound of very minute and reasonably uniform crystals¹⁴. The attainment of this ideal is difficult. The exact methods used in the industrial preparation of precipitated nickel catalysts have usually been regarded as confidential and have not been widely discussed in the literature.

Sodium, potassium and ammonium hydroxides, carbonates and bicarbonates have all been used successfully in the production of precipitated catalysts from nickel sulphate but in the modern practice sodium carbonate and bicarbonate are predominantly used. When these alkalis react with nickel sulphate in aqueous solution, voluminous basic nickel carbonates of variable composition are precipitated. Pure nickel carbonate can be obtained by very special procedures. The pit falls of adsorption and excessive crystal growth are more easily avoided with the use of basic carbonates. The reduction of carbonates proceeds at a lower temperature, minimizing the danger of partially sintering the nickel. These advantages combined with the low cost of sodium carbonate and bicarbonate as precipitants may have conducive effects in the use of this process in industry.

Nickel chloride and nickel nitrate can also be used in the production of precipitated nickel catalysts. In the case of the nitrate, a further advantage is offered in the elimination of absorbed nitrate by thermal decomposition during the reduction step¹⁵.

It has been stated that an economic process^{16,17} has been developed for the recovery of nickel from the spent hydrogenation catalyst in the form of its basic carbonate, hydroxide, sulphate, chloride, and nitrate. It was, therefore, necessary to find out the utility of these salts of nickel for the production of hydrogenation catalyst.

The sulphate, chloride or nitrate either as such in the powder form or after conversion to hydroxide or basic carbonate have been heated at temperatures generally varying from 500°-1000°F in the atmosphere of hydrogen. Since the catalysts prepared by the dry reduction processes are pyrophoric and are difficult to handle, attempts were made to reduce these salts in the oil, as has been done with nickel formate catalyst. But it has been observed that satisfactory reduction of these salts did not take place even at temperatures as high as 270°-280°C and the products have very little catalytic activity. Ellis¹¹ has mentioned that the inorganic salts of nickel can be reduced under pressure to give more satisfactory catalysts. Other investigators¹⁰ have also observed that these salts can undergo reduction at about 250°C, under high pressure of hydrogen. But no detailed information is available in literature as regards the

properties of such catalysts. Therefore it was considered desirable to try the pressure reduction of nickel salts like basic carbonate, and hydroxide and study the activity and selectivity of the catalysts obtained.

EXPERIMENTAL.

Most of the salts of nickel available in the laboratory were studied. All these compounds were of C.P. grade. A few important salts not available in the laboratory were precipitated from nickel sulphate by the precipitation method¹³. From the preliminary investigation of these salts, it was observed that basic carbonate and hydroxide of nickel are most suitable for the preparation of catalyst by pressure reduction. Nitrate and chloride of nickel can also be used for the precipitation of either basic carbonate or hydroxide. In the preparation of catalysts from these salts, hyflo-supercel was used as a support.

Since the activity of the catalyst is dependent upon such operating variables as the temperature of precipitation, the rate of mixing the two solutions and their strength, etc. the basic carbonate of nickel was prepared by three different methods and the properties of nickel catalysts obtained were compared. The three precipitation methods are briefly summarised below.

METHOD I.

It depends upon the precipitation of basic carbonate using concentrated solutions.

Nickel sulphate (86.0 g.) was dissolved in distilled water (200 c.c.) and the solution brought to boil. To this solution, hyflo-supercel (10 g.) was added while a vigorous stirring was maintained. A boiling solution of a chemically equivalent quantity of anhydrous sodium carbonate

(35 g.) in distilled water (100 c.c.) was added drop by drop to the solution of nickel sulphate. The thick flocculent precipitate formed was boiled for about half an hour and then filtered through a sintered glass funnel. After several washings over the funnel with hot distilled water till free from alkali, the precipitate was dried at 100° - 120° overnight, ground, sieved through 100 mesh sieve and stored in a dry bottle.

METHOD II.

It depends upon the precipitation of basic carbonate using dilute solutions.

Nickel sulphate (86 g.) was dissolved in distilled water (4 litres) and the solution brought to boil, when hyflo-supercel (10 g.) was added. The whole mass was kept in uniform suspension by maintaining a vigorous stirring. A boiling solution of anhydrous sodium carbonate (35 g.) in distilled water (1200 c.c.) was added drop by drop to the solution of nickel sulphate in 1.5 hrs. The thick flocculent precipitate formed was boiled for another half an hour, and then filtered through a sintered glass funnel. The precipitate was resuspended in boiling distilled water (4 litres) and filtered. This process was repeated three times till the basic carbonate of nickel was free from alkali. It was then dried at 110° - 120° C overnight, ground, sieved and stored in a dry bottle.

METHOD III.

It depends upon the precipitation of basic carbonate of nickel using dilute solutions with a continuous washing to make the carbonate free from alkali.

The procedure adopted is the same as given in Method II. But the washing technique was slightly modified. The thick flocculent precipitate formed was kept boiling in an enamel bucket while being stirred. An inverted sintered funnel was kept suspended in the bucket and attached to a suction for continuous removal of water. An equal quantity of fresh distilled water was added to the precipitate in the bucket from a jar placed over it. Thus the level of water in the vessel was maintained constant without affecting the dilution of the precipitate. The washing was thus continued for sixteen hours till the basic carbonate was free from alkali. The precipitate was finally filtered through a sintered glass funnel, dried at 110° - 120°C overnight, ground, sieved and stored in a dry bottle.

Similarly nickel nitrate was used for the preparation of basic carbonate of nickel by the first two methods.

Nickel hydroxide was prepared by the addition of a chemically equivalent quantity of ammonium hydroxide to a solution of nickel sulphate (86 g. in 200 c.c.) containing hyflo-supercel (10 g.). The precipitate was filtered through a sintered glass funnel after boiling for about half an hour. It was once washed with hot distilled water, dried at 110° - 120°C overnight, finely ground in a mortar, sieved and stored in a dry bottle.

Assuming that no nickel was lost in the preparations, the above precipitated salts of nickel contained approximately 18-20 gms. of metallic nickel.

Preparation of hydrogenation nickel catalyst by pressure reduction at 100 p.s.i.

Basic nickel carbonate (58 g.) obtained from nickel sulphate by the first method and refined groundnut oil (232 g.) were taken in a laboratory Parrs' medium pressure hydrogenation apparatus described earlier. The speed of agitation was maintained at 525-550 r.p.m. A slow stream of hydrogen was bubbled through the oil-nickel carbonate mixture. The residual gases were allowed to escape through the vent cock. The contents in the autoclave were heated to 150°C when the initial reaction began. The temperature was maintained at about 190°C until this preliminary activity in reduction was over and moisture driven off. The temperature of the autoclave was then slowly raised to 250°C. The vent cock was then closed and the hydrogen pressure raised to 100 p.s.i. The gases produced due to reduction of the nickel salt were vented at regular intervals. As soon as the reduction of basic nickel carbonate was over, the oil started hydrogenating rapidly. The charge was maintained at 250°C and 100 p.s.i. for about 4 hrs. when the catalyst became dark grey in colour and no green particles were visible. At this stage there was no further appreciable consumption of hydrogen. The heat was then turned off, but the agitation and the pressure of hydrogen were maintained during the cooling operation. When the catalyst charge cooled down below 100°C, it was removed from the autoclave. The excess of oil from oil-nickel catalyst mixture was filtered through a double No.1 Whatman filter paper in a hot filter funnel so that the concentration of nickel in the congealed catalyst cake was about 25 per cent.

Similarly five more samples of catalysts were prepared, four from basic nickel carbonates and one from nickel hydroxide obtained by the various precipitation methods described above.

Preparation of hydrogenation nickel catalyst by pressure reduction at 300 p.s.i.

In order to study the effect of reduction pressure on the activity of nickel catalyst obtained by the wet-process a sample of basic nickel carbonate obtained from nickel sulphate by the precipitation method of concentrated solutions (Method I) was reduced under a hydrogen pressure of 300 p.s.i.

The comparative activities of the above seven samples of nickel catalysts were tested by using them for the hydrogenation of refined groundnut oil (500 g.) in the Parr's medium pressure hydrogenation apparatus. The hydrogenation conditions of temperature, pressure and catalyst concentration were the same as standardized when the catalyst obtained from nickel formate (Chapters I and II) was used.

The characteristics of the various products obtained are reported in Table X.

OBSERVATIONS.

From these results it may be seen that the catalyst obtained from basic nickel carbonate precipitated by the continuous washing procedure (Method III) is superior to those obtained either by the precipitated method of concentrated solutions (Method I) or by the method of dilute solutions (Method II). Further, the catalyst prepared in concentrated solutions is superior to that obtained in dilute solutions.

A reduction pressure of 100 p.s.i. is preferable to the higher pressure of 300 p.s.i. for the decomposition of nickel salts into nickel catalysts.

The catalyst obtained from nickel sulphate is better than that obtained from nickel nitrate if selectivity of hydrogenation is considered. This may be due to the presence of traces of sulphate ions present in the catalyst.

The catalyst from basic carbonate is to some extent superior to that obtained from nickel hydroxide both as regards the consistency of the product and selectivity of hydrogenation.

Conclusions

Besides the formate, the basic carbonate of nickel prepared from sulphate in dilute solutions using a continuous washing technique and supported on a neutral carrier as hyflo-superpel when reduced under a moderate pressure of 100 p.s.i. at a temperature of 245°-250°C by wet reduction process gives a catalyst by the use of which a hydrogenated product of satisfactory consistency and selectivity can be obtained. The activity of such a catalyst is comparable with that obtained from nickel formate.

*

TABLE X.

Characteristics of hydrogenated groundnut using catalysts from salts of nickel other than formate.

Nickel salt used in catalyst preparation	Pressure of reduction of the salt lbs.p.s.i.	Hydrogenation time			Congeal point °C	Penetration (dial reading)	Butyro-refractometer reading 400C.	Iodine value (Wt%)	Titer value %	Component fatty acids %			
		hr.	min.	sec.						Saturated acids	Iso-oleic acids	Linoleic acid	Oleic acid.
Basic carbonate from sulphate (conc. solution)	100	3	20	30.2	42	51.1	60.0	38.8	30.0	22.0	0.4	47.5	
"	300	2	30	29.8	soft	54.3	72.5	34.2	24.7	23.5	6.1	45.6	
Basic carbonate from nitrate (conc. solution)	100	3	20	24.2	140	52.2	62.5	34.6	27.7	14.9	3.5	53.9	
Basic carbonate from sulphate (dilute solution)	100	3	50	23.7	156	52.4	64.7	34.1	25.8	12.8	3.0	58.4	
Basic carbonate from nitrate (dilute solution)	100	3	45	24.4	120	51.8	63.4	34.9	27.6	15.2	3.1	54.1	
Hydroxide from sulphate (conc. solution)	100	3	0	30.4	61	51.0	69.1	39.4	32.5	18.1	1.8	47.6	
Basic carbonate from sulphate (dilute solution and continuous washing)	100	2	15	30.6	35	52.5	63.7	33.8	31.5	36.3	.0	32.2	

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CHAPTER V.

EFFECT OF OTHER METALS ON THE ACTIVITY OF NICKEL CATALYST

Numerous instances are known in which the activity of a catalyst is increased by the addition of a substance in small amounts. Ipatieff¹ was the first to discover the accelerating effect of small quantities of iron in the catalytic reduction of anylene to the hexahydro compound by means of oxide of copper. Dewar and Liebmann² prepared the catalyst required for the hydrogenation of fixed oils from a mixture of the oxides, hydroxides, cobalt, copper and iron with or without the addition of silver oxide. Taylor³ states that the addition of copper to the nickel catalyst increases the life of the catalyst and renders it less susceptible to poisons. Kahlenberg and Ritter⁴ claim that a catalyst containing equal weights of nickel and cobalt is more active than either metal when used alone. Ellis⁵ reported that the hydrogenation can be carried out rapidly and at comparatively low temperatures by adding an oxide of some rare metal which reduces with difficulty to any of the catalysts, iron, nickel, cobalt, or copper.

Opposite views are, however, held by Armstrong and Hilditch⁶. They state that nickel-copper catalysts prepared at 180°C are not so active as plain nickel catalysts produced from basic carbonate of nickel by reduction at higher temperatures. Patel⁷ also states that the presence of metals like cobalt, silver and copper in nickel catalyst have an inhibiting effect on its activity.

Ellis⁵ recommends the use of salts containing carbon such as carbonates or formates for the preparation of active catalyst either as such or in the promoted form. The proportion of the components employed in the catalytic mixture may be varied considerably. Even an addition of one per cent or less of the promoter has been stated to produce favourable action. The use of mixtures containing strongly basic bodies in the hydrogenation of fats has been found undesirable.

Medsforth⁸ has stated that as it is difficult to secure a uniform deposit of the catalyst and promoter of the same composition on the carrier, concordant results cannot be expected. He also observed that promoters may act selectively.

William and Taylor⁹ also believe in the selectiveness of the promoters. The function of the majority of the promoters according to them is simply to increase the available surface of the catalyst. Similar view points are held by Armstrong and Hilditch⁶. Glass and Kahlenberg¹⁰ concluded that those materials which inhibit the catalytic activity of platinum and palladium have been found to affect nickel similarly. The behaviour of the supports with relation to the hydrogenation of cottonseed oil by nickel can be classified as follows. Reducible heavy metal oxides completely inhibit the activity of nickel. The salts of those metals that decompose on heating in a stream of hydrogen completely inhibit activity. Substances with corrosive properties retard but do not completely inhibit activity. The more inert the support

becomes towards nickel, the greater is its tendency to enhance activity.

Present work

The effect of other metals on the activity of nickel catalyst has so far been investigated by various workers using dry reduction technique involving temperature between 325 and 450°C¹⁰. As has been stated earlier, the catalysts prepared by this procedure are pyrophoric in nature and their activities are difficult to control. It was, therefore, considered worthwhile to investigate the behaviour of other metals on the activity and selectivity of nickel catalyst when prepared from basic carbonate by wet reduction process.

Since Ellis⁵ has pointed out that excessive amounts of the promoter reduces the exposed surface of the catalyst and may have adverse effect on its activity, salts of various metals, the effect of which were to be investigated, were taken in such amounts that the metals did not form more than 10 per cent of the nickel catalyst. Salts of copper, calcium, barium, strontium, lithium, and calcium and magnesium mixture (1:1) were added to nickel salt in amounts so as to give about 10 per cent of metal on the available nickel. Similarly salts of titanium, iron, manganese, chromium, aluminium and cobalt were to get about 5 per cent, while silver and other rare earth salts were taken to get only 0.1 per cent metal on the weight of the nickel catalyst. For the preparation of the metal-nickel catalyst, the procedure of preparing the basic carbonate in concentrated solutions described in Chapter IV was employed as it is more

rapid than the continuous washing method inspite of the fact that the catalyst prepared from the basic carbonate of nickel obtained by the latter is the most efficient found so far. As an illustration, the method of co-precipitating copper and basic nickel carbonate is described as follows.

EXPERIMENTAL.

Nickel sulphate (91 g.) and copper sulphate (8.7 g.) were dissolved in distilled water (200 c.c.) and the solution boiled. To this solution hyflo-supercel (10 g.) was added while a vigorous stirring was maintained to keep the mass in well suspension. A hot solution of sodium carbonate (40 g.) in distilled water (100 c.c.) was slowly added drop by drop to the copper-nickel solution. The thick flocculent precipitate formed was boiled for about half an hour and then filtered through a sintered glass funnel. After several washings on the funnel with hot distilled water till free from alkali, the precipitate was dried at 110°-120°C overnight, ground, sieved through 100 mesh sieve and stored in a dry bottle.

The other promoters were co-precipitated with nickel in a similar manner using mostly chlorides of the metals.

Armstrong and Hilditch⁶ have stated that a somewhat incomplete precipitation of copper by alkaline carbonate is essential, for they found that a very close connection existed between the precipitates giving rise to active catalysts and the class of compounds termed by Pickering α -cupricarbonates $\text{Na}_2\text{Cu}(\text{CO}_3)_2$. On the basis of their findings, one experiment was conducted in which copper sulphate and nickel sulphate were incompletely precipitated by reducing the quantity of sodium carbonate to 30 grams and corresponding reduction of hyflo-supercel to 7.5 grams.

A sample of aluminium-nickel catalyst was prepared by the method described by Bailey¹¹ as follows.

Sodium hydroxide 16 Be° (36 g.) was added to a mixture of aluminium powder (15 g.) and hyflo-supercel (10 g.). When the foaming subsided, a solution of sodium carbonate (57 g.) was added and the mixture made up to 2 litres with distilled water. It was then added to the nickel nitrate solution prepared by dissolving 100 gms. of the salt in distilled water (4 litres) over a period of 1.5 hrs. The temperature of the bath was raised from 65°C. to boiling. The precipitated catalyst was filtered, resuspended in hot distilled water (4 litres), again filtered and the process of washing repeated twice till when it was free from alkali. The precipitate was dried at 110°-120°C overnight, ground, sieved through 100 mesh sieve and stored in a dry bottle.

The various co-precipitated basic carbonates obtained as above were reduced for the preparation of the catalysts by wet reduction process described earlier (Chapter IV). The reduction pressure of hydrogen was maintained at 100 p.s.i. during the process. The reduction was considered as completed when no further absorption of hydrogen took place as indicated by the pressure gauge. This took about 4-5 hours. The excess of oil was filtered off so that the nickel content in the catalyst cake was about 25 per cent.

All the precipitated nickel catalyst were tested for their effectiveness by conducting the hydrogenation of refined groundnut oil (500 g.) in the Parr's hydrogenation

apparatus described earlier. The catalysts were taken in such amounts as to give 0.2 per cent nickel on the weight of the oil. Hyflo-supercel (2 g.) was also added. The temperature 180°C . and pressure 85-90 p.s.i. were maintained during the process. The hydrogenation was considered as completed when the fat attained a slip point $36^{\circ}\text{-}37^{\circ}\text{C}$. The fat was then filtered and the catalyst removed. The characteristics of the products obtained by using nickel catalysts co-precipitated with various metals are given in Table XI.

Observations:

From these results, it may be seen that taking the time of hydrogenation of the oil to the slip point $36^{\circ}\text{-}37^{\circ}\text{C}$, all the metals except molybdenum, silver and chromium have behaved as retarders for the activity of the nickel catalyst. This may be due to the fact that the catalyst in the present investigation have been prepared by wet reduction process at the minimum temperature of 250°C as against the dry reduction process employed by previous workers. Even with the three metals found to be promoters as regards rate of hydrogenation is considered (item 18-20) - Table XI), the consistency of the products and the selectivity of hydrogenation have not been quite satisfactory. As chromium is the cheapest and most easily available metal of these three promoters, smaller quantities e.g. 1.0 and 0.5 per cent on the weight of the nickel catalyst were tried. As may be seen from the data in items 21 and 22 of the above Table, almost similar types of products were obtained as when 5.0 per cent of the metal was used as a promoter.

Basic carbonate of nickel co-precipitated with chromium salt (5.0% metal) was prepared by continuous washing procedure described in Chapter IV. The chromium-nickel catalyst from the mixed salt was prepared by wet reduction process under 100 p.s.i. hydrogen pressure by the usual method. This catalyst was used for the hydrogenation of groundnut oil under the conditions already mentioned. The hydrogenated product obtained was found to have good consistency. Its fatty acid composition (item 23 Table XI) was almost similar to that when nickel catalyst from nickel formate was used.

Conclusions:

The continuous washing procedure might have caused advantage in the preparation of the catalyst, that, besides the complete washing of the alkali from the precipitated basic carbonates of the metals, the requisite crystalline form of the crystals is maintained.

TABLE XI.

Effect of various metals on activity of nickel as obtained with the hydrogenation of groundnut oil

No	Name of the co-precipitated metal	Per cent on nickel	Hydrogenation time hrs.	Congeal point °C	Penetration (dial reading) mm/10	Butyro-refractometer reading 40°C.	Iodine value (Wt%)	Titer value 0°C	Component fatty acids				
									Saturated acids %	Iso-oelic acids %	Linoleic Acids %	Oleic acid %	
1.	Nil (control using nickel alone)	--	3	20	30.2	42	51.2	60	38.8	30.0	22.0	0.4	47.5
2.	Iron (ic)	5.0	6	30	20	liquid	56.7	86.3	32.4	18.2	3.4	20.6	57.0
3.	Manganese (ous)	5.0	6	30	20	liquid	56.3	84.1	32.2	19.0	2.1	19.0	59.9
4.	Titanium (ous)	5.0	6	15	20	semi-solid	53.2	68.5	33.1	23.2	8.7	3.4	64.7
5.	Cobalt (ous)	5.0	6	15	22.0	180	55.2	78.2	32.5	21.2	8.9	12.9	57.0
6.	Copper (ic)	10.0	5	30	20	liquid	55.5	80.1	32.6	20.6	5.3	14.8	59.3
7.	Copper (incomplete precipitation method)	10.0	5	30	21.8	214	54.5	74.7	32.8	21.4	7.4	8.6	62.6
8.	Strontium	10.0	5	0	20	liquid	57.3	89.3	31.5	16.1	1.4	23.3	59.2
9.	Calcium	10.0	5	0	20	liquid	56.7	86.4	32.3	17.8	2.4	20.5	59.3
10.	Barium	10.0	4	20	21.6	277	53.3	69.4	32.7	24.6	9.8	4.3	61.3
11.	Calcium magnesium	5.5	4	15	22.1	176	52.2	63.8	36.6	26.4	14.3	nil	59.3
12.	Beryllium	0.1	4	15	20.1	330	52.7	66.3	33.3	22.8	10.4	4.9	61.9
13.	Cerium (ous)	0.1	4	0	20	liquid	55.9	82.3	32.4	19.3	4.2	16.6	59.9
14.	Lithium	10.0	4	0	21.7	247	52.3	64.2	36.4	27.2	11.6	nil	61.2
15.	Aluminium Bailey's Method	5.0	4	0	21.9	liquid	52.7	66.0	33.4	16.4	9.7	1.9	72.0
16.	Aluminium	5.0	3	30	20	liquid	51.9	62.2	36.8	17.7	9.9	nil	72.4

.....continued

TABLE XI (continued)

17. Thorium	0.1	3	30	20	semi- solid	52.7	66.5	33.2	22.8	10.4	4.9	61.9
18. Molybdenum	0.1	2	45	24.4	120	51.3	60.4	35.4	27.5	12.0	nil	60.5
19. Silver	0.1	2	30	24.3	125	51.3	60.5	35.8	28.1	12.5	nil	59.4
20. Chromium	5.0	2	15	20	semi- solid	52.5	65.1	33.4	23.4	11.6	nil	65.0
21. Chromium	1.0	2	15	21.8	"	52.3	64.3	32.4	26.4	14.3	nil	59.3
22. Chromium	0.5	2	30	22.2	176	52.2	63.7	36.0	27.3	15.4	nil	57.3
23. Chromium (continuous washing)	5.0	2	0	31.8	24	52.0	62.5	37.1	24.7	30.6	nil	44.7

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CHAPTER VI.

DETERMINATION OF TRANS-ISOOLEIC ACIDS IN THE HYDROGENATED FATS.

The quantitative determination of isooleic acids contents in partially hydrogenated fats is of great importance because these acids contribute to the body of the product at low temperatures.

Moore¹ observed the presence of solid isooleic acids in various hydrogenated fats. He examined ethyl oleates which had been partially hydrogenated. He concluded that the solid iso-oleic acids were composed of $\triangle^{9,10}$ -, $\triangle^{11,12}$ --, and possibly $\triangle^{10,11}$ --, iso-oleic acids. The $\triangle^{9,10}$ -, isomer was considered to be elaidic acid. He believed that the above two positional isomers probably also possessed trans configurations.

Hilditch and Vidyarthi² reported that in the hydrogenation of methyl oleate, both $\triangle^{8,9}$ -, and $\triangle^{10,11}$ oleic acids and their trans-modifications in addition to some elaidic acid are formed. So both Moore¹ and Hilditch and Vidyarthi found that during the partial hydrogenation of alkyl oleates, both geometrical and positional isomers are formed.

The American Oil Chemist's Society recommend the modified Twitchell lead salt-alcohol method³ for the determination of iso-oleic acids in fatty acid mixtures.

Swern and co-workers⁴ developed a method for determination of trans octadecenoic acids and related compounds, based on the quantitative measurement of absorption

at 10.36 μ . They compared the infra-red method with the lead salt alcohol method of determining trans-octadecenoic acids in mixtures with cis-isomers and saturated acids and found that the former was more rapid, specific and accurate than the latter method. They observed that by the lead salt alcohol method, the results in most cases differed widely from those obtained by the infra-red spectrophotometric technique. Trans octadecenoic acids are not determined quantitatively by the Twitchell lead salt alcohol method. The results are always low by this procedure. Moreover when large amounts of cis-acids are present, these are also isolated partially with the solid acid fraction.

Jackson and Callen⁵ also compared the lead salt-alcohol method with the infra-red method and confirmed the greater accuracy and convenience of the latter procedure. The Twitchell method is fairly satisfactory for simple elaidic-oleic acid mixture but gives very low values with ordinary hydrogenated fat acids. The reason for this failure has been attributed to the increasing solubility of lead iso-oleate with the increase in the number of trans iso-oleic acids.

Cocks, Christian and Harding⁶ have suggested a modification of the Twitchell method, involving the use of petroleum ether (40-60°) in conjunction with the formation of lead salts in alcohol for the more accurate determination of iso-oleic acids in fatty acid mixtures.

Although the infra-red spectrophotometric method has been found to be rapid, specific and accurate for the estimation of trans iso-oleic acids in fatty acid mixtures, it requires special equipment which is not always available. During the investigations on the modification of nickel catalyst for the hydrogenation of oils carried out in this laboratory and summarised in the earlier chapters, the amount of iso-oleic acids in various hydrogenated samples of groundnut and cottonseed oils have been determined by the method of Cocks⁶. The results have generally been found to be in close agreement with those obtained by the infra-red spectrophotometric method, showing thereby that the method of Cocks, Christian and Harding⁶ may alternatively be employed for the accurate determination of trans iso-oleic acids in hydrogenated fats.

E_X_P_E_R_I_M_E_N_T_A_L.

The fatty acids of the partially hydrogenated groundnut and cottonseed oil samples referred to in previous chapters were prepared by the usual saponification procedure as follows.

Hydrogenated fat (50 g.) was saponified with a solution of potassium hydroxide (15 g.) in 95% ethyl alcohol (250 c.c.), the solution was boiled freely under reflux reflux condenser for 3 hrs., and the excess of alcohol recovered by distillation. The soap was dissolved in distilled water and after removal of unsaponifiable matter, was converted into the free fatty acids by warming with sulphuric acid (1:1). The liberated acids were extracted with petroleum ether (60-80°), the ether extract, washed free of mineral acid, dried over anhydrous sodium sulphate and filtered. The mixed fatty-acids recovered by removal of petroleum ether were eventually dried under vacuum at 100°C.

The determination of iso-oleic acids in the various samples of hydrogenated fat was carried out in duplicate by the method of Cocks et al⁶ as follows.

In all cases a quantity of 3.5 gms. of the freshly prepared fatty acids was dissolved in 50 c.c. of 92-93 per cent alcohol and 3.45 gms. of lead acetate, $Pb(CH_3COO)_2 \cdot 3H_2O$, was separately dissolved in 50 c.c. of similar alcohol. Both the solutions were heated to boiling point and that containing the lead acetate was poured into one containing the fatty-acids. After mixing and again heating to boiling, the solution was allowed to cool slowly and kept overnight

The next morning the mixture was stirred and filtered from the alcohol as completely as possible on a 10 cm. Buchner funnel, which was then transferred to a clean filter flask. The lead salts on the Buchner funnel and any remaining in the precipitating vessel was washed with 100 c.c. of petroleum ether (40° - 60°) using amounts of 20 c.c. at a time, and the washings were then distilled from a water-bath to remove the petroleum ether completely. The residue was redissolved by boiling under a reflux condenser with 20 c.c. of 92-93 per cent alcohol containing one drop (0.5 g.) of glacial acetic acid. The solution was allowed to crystallize at 15°C for 3 hours. The lead salts of the solid acids were filtered and washed with 20 c.c. of cold 92-93 per cent alcohol. The solids remaining behind on the filter paper were worked up with the main bulk of the lead salts of the solid acids. Finally they were decomposed with dilute nitric acid in the presence of ethyl ether, washed the latter free from mineral acid and dried over anhydrous sodium sulphate. The solid acids were recovered by the removal of the solvent and eventually dried under vacuum at 100°C . The total solid acids were weighed, a portion was used for iodine value determination from which the amounts of solid saturated and solid unsaturated acids were calculated.

The values of the unsaturated solid acids were checked by the infra-red spectrophotometric method for which a Grubb Parsons spectrometer of the single beam type with a sodium chloride prism was used. Determinations were made using a fixed slit 0.2 mm. and a 0.1 mm. sodium chloride cell. The fatty acids of hydrogenated fats were examined as

solutions of known concentrations in purified carbon bisulphide. The base line technique of Wright⁷ and Heigl, Bell and White⁸ was used for the measurement of optical densities. It has been shown by Rasmusson⁹ and Swern⁴ that trans-monounsaturated compounds have a strong characteristic absorption at 10.36 μ unlike cis and saturated compounds. A calibration curve (Fig. 1) of elaidic acid (B.D.H.) was obtained by plotting its known concentrations in carbon bisulphide against their optical densities which were determined by finding out the per centage absorptions at 10.36 μ . Extinction coefficient, K, was calculated from the formula $K = \frac{d}{c \cdot l}$, where d is the optical density, c is concentration in g/litre and l is cell thickness in cm.

The extinction coefficient (K) for pure elaidic acid has been found to be 0.593. The extinction coefficients of the acids of hydrogenated fats at 10.36 μ were obtained as above and from these values and that of pure elaidic acid, the per centages of trans-isooleic acids in various samples were calculated. For each sample, six values were independently taken and the mean result recorded.

The per centages of iso-oleic acids in various samples of hydrogenated groundnut and cottonseed oils found by both the chemical and spectrophotometric methods have been reported in Tables XII. and XIII.

DISCUSSION AND CONCLUSION.

From the data given in the above two Tables, it is seen that, with the exception of five results (Table XII.), there is a fair agreement between the amounts of iso-oleic acids as determined by infra-red spectroscopic method and by Cocks et al⁶ chemical procedure in various samples of hydrogenated fats. Even in the results of five samples, the variations between the two values have not been more than 6.5 per cent. The chances of separation of the lead salts of the various isomers of cis and mono-ethenoid C₁₈-acids formed as a result of shifting of the double bond of oleic acid or due to hydrogenation of linoleic acids are greatly minimized because at first the cis-positional isomers are formed much less than the trans ones¹⁰. Secondly the lead salts of the isomeric solid oleic acids were found by Hilditch and Vidyarthi² closely similar in solubility so that little or no separation results. In fact $\triangle^{8:9}$, and $\triangle^{10:11}$ -, octadecenoic acids were found by them as to furnish the soluble lead salts. Further the data in Tables XII. and XIII. clearly show that in cases where the results by Cocks method were higher than the infra-red procedure, the differences were of minor nature and remained within the experimental error.

Therefore, the Twitchell lead salt alcohol procedure as modified by Cocks, Christian and Harding⁶ may be recommended as an alternative procedure for the determination of trans isocoleic acids in the hydrogenated fats, where more accurate infra-red absorption procedure is not available.

*

TABLE XII

Trans Iso-oleic acids in the fatty acids of various samples of hydrogenated groundnut oil.

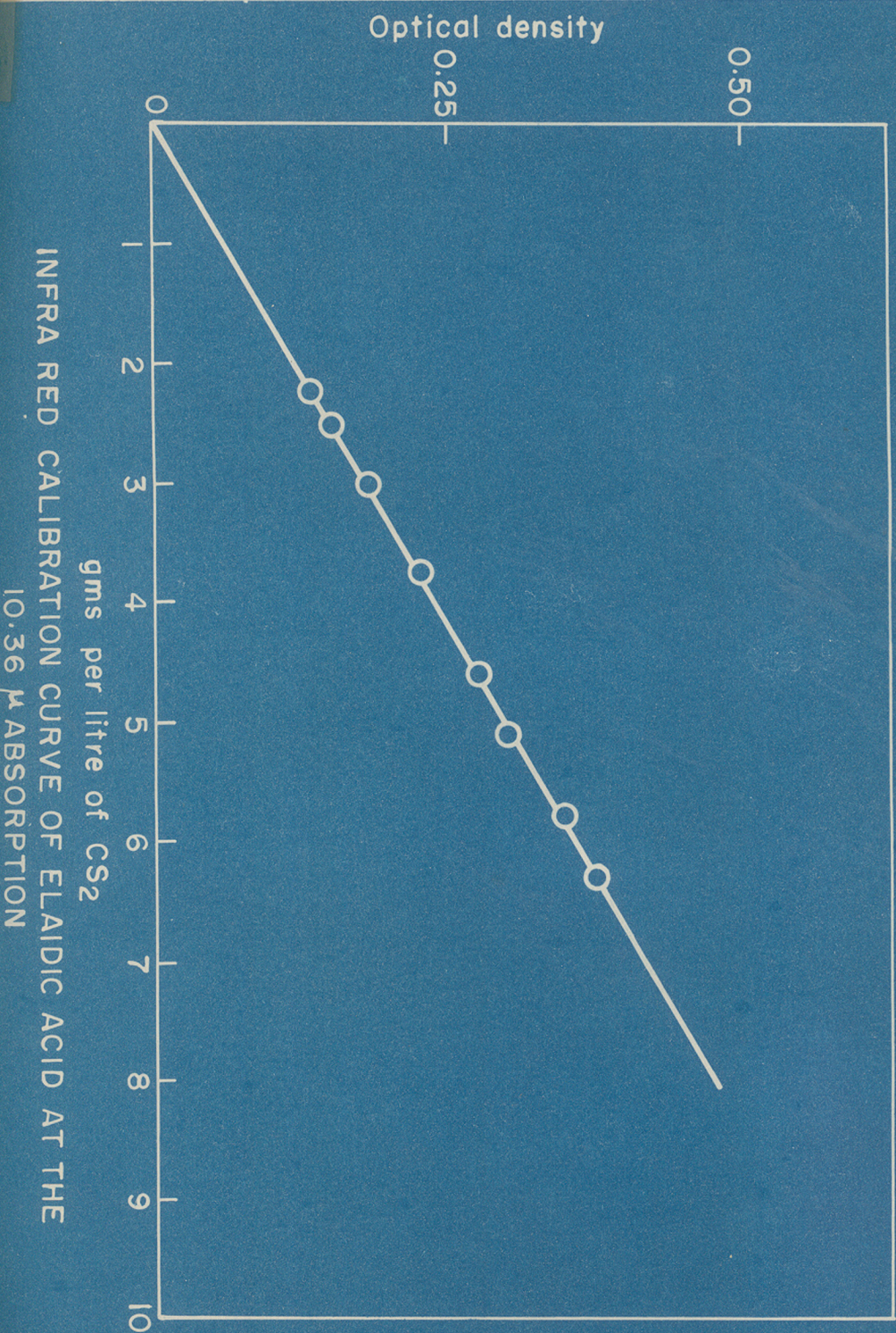
Trans Iso-oleic acids in fatty acids samples		Variation of Cocks
Infra-red method	Cocks et al method	value from infra-red value
%	%	%
40.75	41.22	+1.1
32.94	33.70	+2.3
30.20	28.37	-6.0
5.20	4.88	-6.1
18.50	17.30	-6.5
31.70	31.67	-0.1
29.87	29.71	-0.5
24.98	25.33	+1.4
35.80	35.46	-0.9
24.58	24.47	-0.4
31.50	32.14	+2.0
28.02	28.20	+0.6
25.68	25.90	+0.8
35.80	35.46	-0.9
24.56	24.66	+0.2
26.54	26.60	+0.2
36.48	36.60	+0.3
30.89	30.80	-0.3
41.14	40.96	-0.4
30.95	30.70	-0.8
35.82	35.96	+0.4
25.72	26.10	+1.5
33.92	33.55	-1.1
28.72	27.31	-4.9
24.75	25.50	+3.0
40.10	37.80	-5.8
34.25	35.46	+3.5
37.16	37.80	+1.7
37.11	37.85	+2.0
32.99	33.68	+2.1
33.20	33.63	+1.3
36.09	36.53	+1.2

Note: The first three were commercial brands of vanaspati samples.

TABLE XIII.

Trans-Iso-oleic acids in the fatty acids of various samples of hydrogenated cottonseed oil.

Trans Iso-oleic acids in fatty acid samples		Variation of Cocks value from infra-red value %
Infra-red method %	Cocks et al method %	
42.82	43.17	+0.8
39.97	40.55	+1.5
44.84	44.69	-0.3
46.47	46.51	+0.9



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PART B.

APPLICATION OF N-BROMOSUCCINIMIDE FOR THE CREATION

OF CONJUGATION IN FATTY ACIDS

AND OILS.

CHAPTER VII.

APPLICATION OF N-BROMOSUCCINIMIDE IN THE PRODUCTION OF CONJUGATION IN FATTY-ACIDS AND OILS.

I_N_T_R_O_D_U_C_T_I_O_N.

The recognised benefits of conjugated unsaturation in drying oils and the continued shortage and high price of conjugated oils (tung oil) have focussed the attention of chemists and technologists alike upon ways and means of providing adequate supplies of drying oils of this type at more reasonable cost.

When two or more double bonds are present in the same fatty-acid, the opportunity for the occurrence of positional isomers is increased. However, only a few such isomers have been observed in natural fats and most of these belong to the trienoic acid series. In addition to these natural isomers, other positional isomers of linoleic acid are produced by a variety of chemical reactions, several of which are of industrial importance. Further it has been found that, if the double bonds are situated in conjugated position, the importance of isomeric polyethenoid acids increases considerably. Thus methods of creation of new double bonds in conjugated position for developing drying properties in fatty oils or acids of low unsaturation have been frequently reported. They are summarised below.

METHODS OF CREATING CONJUGATION IN UNSATURATED ACIDS.

Isomerisation of double bonds:- Moore¹ observed that the fatty-acids produced by prolonged saponification with potassium hydroxide of fats containing ordinary linoleic acid, exhibited ultra-violet absorption maximum at 230 mu. which is characteristic of the presence of conjugated double bonds. It was later established by Kass and Burr² that when equal weights of linoleic acid and potassium hydroxide were heated for two hours with four volumes of ethylene glycol, the linoleic acid was converted into a crystalline acid, m.p.79°C; ester m.p.41°C. On the basis of disruptive oxidation, the acid was identified as $\Delta^{-10:11, 12:13, 14:15}$ -octadecatrienoic acid, and hence a positional isomer of naturally occurring elaeostearic acid. This acid was designated as pseudo-elaeostearic acid.

The isomerisation of polyunsaturated fatty-acids can be affected in the presence of a solvent, by heat and the catalytic action of alkalies, siliceous earths, metallic oxides and various other catalysts. Turk and Feldman³ have described the use of siliceous materials as catalysts for the isomerisation of double bonds in unsaturated fatty oils and acids so as to produce conjugation. Scheiber⁴ mentioned the use of metallic oxides (aluminium and mercury oxides) as isomerising catalysts. Turk and Boone⁵ used activated alumina, aluminium oxide, and some oxides of groups IV and VIA of the periodic system for the same purpose. They observed that the physical properties of the catalytic materials constitute a significant factor in

determining the extent of the isomerisation reaction.

The isomerised oils which have recently appeared on the market in the United States are prepared by treating oils containing linoleic and linolenic acids in such a manner as to induce a shift in the double bonds of these acids to conjugated positions. These oils, like dehydrated castor oil, are substituted for tung oil. Most of the isomerised oils are made from soybean and linseed oils by alkali isomerisation process developed by Bradly and Richardson⁶. They have described a process which has enabled the formation of 30 to 50 per cent of conjugated acids from soybean and linseed oils. Such acids have been found to be useful for the production of improved drying oils and resins. This process is uneconomical as it consists essentially of reacting the fatty-acids of the oil with an excess of aqueous alkali solution at a high temperature (425°-450°F) and re-esterifying the resulting isomerised acids with glycerol.

Mitchell and Kraybill⁷ observed that the absorption spectra of linseed, soybean, corn and cottonseed oils, and the esters of linoleic and linolenic acids were quite dissimilar before and after bleaching with fuller's earth. Linoleic acid and the oils containing the above acids, when subjected to the action of bleaching earths, were found to have developed a specific absorption maximum at 268 mμ which is characteristic of triene conjugation. If the acid or oil is first oxidized by blowing it with air at 100°C and then bleached with fuller's earth, the concentration of triene conjugation is increased. The authors conclude, therefore, that the action of bleaching earths results in

dehydration of pre-existing oxygenated acids or of similar acids which may be produced by blowing the oil with air.

Debromination of tetrabromostearic acids:- Brode and co-workers⁸ have shown that the nature of the linoleic acid produced on debromination of tetrabromostearic acids depended upon the original tetrabromostearic acids and the method of debromination. The regenerated acids were generally found to consist of mixtures of conjugated and non-conjugated linoleic acids, and in some cases consists of small amounts of triene and tetraene conjugated acids also. The formation of conjugated acids on debromination was attributed by these authors to the catalytic isomerisation action of zinc bromide formed during debromination.

Creation of double bond by dehydration:- Schieber⁴ in 1931 found that when ricinoleic acid is heated at about 300°C, the hydroxyl group at the 12th position takes an atom of hydrogen either from the 11th carbon atom or the 13th of the molecule and is removed as water leading to the formation of 9:11- and 9:12- linoleic acids. When these acids are esterified with glycerine, an oil of good drying properties is obtained. The process was subsequently applied to the castor oil itself for the formation of dehydrated castor oil. Although schieber claimed that the constituent fatty acids consisted upto 90% of the conjugated acid, this claim, however, has not been substantiated and not more than one third of the ricinoleic acid changes to 9:11-linoleic acid. Side by side with the formation of dehydrated castor oil, decomposition of the oil takes place to some extent with the production of heptaldehyde, undecenoic acid, octylene, sebacic

acid, semi-aldehyde, acrolein, myristic, palmitic, stearic and oleic acids. To reduce these decompositions to the minimum, it is, therefore, necessary to keep the temperature below 280°C and since the rate of dehydration is slow at this temperature, to use a catalyst. Numerous catalysts have been employed for this purpose. Sulphuric and phosphoric acids and their acid salts have been used with success. The other catalysts are: oxides of metals as aluminium, zinc, tungsten, persulphates, sulphonic acids, etheionic acid, chlorides of iron, zinc, calcium, silicon, phosphorus etc. The catalysts besides helping in the dehydration of the oil should be such as to give the minimum of decarboxylation of the oil.

Dehydrated castor oil is used extensively in the formulation of paints and varnishes and in the manufacture of linoleum. Its film is superior to linseed oil comparing quite favourably in certain respects to that of tung oil.

Isomerised oils are also prepared by the introduction of hydroxyl groups by oxidation accompanied by dehydration⁹. The method of oxidation and dehydration is commonly used for the preparation of synthetic or modified drying oils from oils rich in oleic acid, soybean and linseed oils by blowing them with air or treatment with other oxidising agents, followed by catalytic dehydration. The dehydration reaction leads to the formation of additional double bonds in both the linoleic and linolenic acids which are present in these oils. At least a portion of the newly introduced double bond is conjugated with the other double bond.

Munzel process:- A process for making a triple-unsaturated conjugated ester from castor oil using a freshly precipitated tungstic acid anhydride was reported by Munzel¹⁰. Munzel process claims the production of mostly conjugated dehydrated castor oil from the raw oil. Dehydrated castor oil is known as dienol, which is then treated with hypochlorous acid when hydroxyl group of hypochlorous acid adds to the 9th carbon atom and chlorine atom to the 12th carbon atom. Removal of hydrochloric acid and water gives a triple unsaturated conjugated ester.

Creation of double bond by dehydrochlorination: The isomerisation can also be brought essentially through chlorination followed by dehydrochlorination as shown by Gardner and Bielouss¹¹. Details of this process are under patent literature.

Allylic chlorination with tert-butyl hypochlorite: Teeter and co-workers¹² have carried out allylic chlorination with tert-butyl hypochlorite of methyl oleate, methyl linoleate and some vegetable oils under varied conditions of reaction and through thermal dehydrochlorination introduced conjugation, principally of diene and triene type. In the case of methyl oleate, they found that the products consisted mostly a mixture of allylic and non-allylic mono-chloro derivatives and a saturated dichloro derivative possibly methyl 9:10-dichloro stearate. Methyl linoleate was converted by tert-butyl hypochlorite and methanol to methyl dimethoxy dichlorostearate and its thermal decomposition resulted in the formation of 21.7% methyl diketo stearate. They have explained all these reactions via a free-radical chain process. More recently, Arnold¹³ has

taken a patent on the use of metal hypochlorite for the same purpose.

Wohl-Ziegler reaction:- Wohl¹⁴ introduced a method for the direct addition of a halogen atom (Bromine) in the allylic position of an olefin by means of N-bromoacetamide. In 1942, Ziegler et al¹⁵ published their extensive researches on the allylic bromination of olefins by means of N-bromosuccinimide. This reaction is now commonly known as Wohl-Ziegler reaction. Ziegler et al¹⁵ have shown that a hydrogen atom on a methylene group adjacent to an ethylenic double bond is substituted via a free-radical chain mechanism.

Teeter¹⁶ applied the Wohl-Ziegler reaction to esters of soybean fatty acids and methyl linoleate. He introduced bromine in the allylic position in methyl esters of these fatty-acids. He further investigated the reactions of the brominated esters with sodium methoxide, cuprous cyanide, and sodium cyanide.

Schmid and Lehman¹⁷ brominated methyl elaidate and methyl brassidate with N-bromosuccinimide and after dehydrobromination isolated $\Delta^{9:12}$ -octadecadienoic and $\Delta^{13:15}$ -docosadienoic acids. They used equimolecular proportions of N-bromosuccinimide and methyl ester of mono-olefinic acid. Gunstone¹⁸ has, however, pointed out that the properties of the former acid differ from those of the known trans-trans 9,11-octadeca-dienoic acid and call for confirmation of these results.

From their experiments on the bromination of methyl oleate with equimolecular proportion of N-bromosuccinimide and subsequent permanganate oxidation of the brominated products, Suttan and Dutta¹⁹ observed that both the 9- and 11-mono-bromo-oleates together with a small quantity of dibromoester were formed. They, however, could not separate the two monobromo isomers in pure state.

Clemo and Stevens treated methyl petroselinate with N-bromosuccinimide and obtained an oily monobromo-compound. Its dehydrobromination by collidine gave a product shown by ozonolysis and unsaturation to be octadeca-6:8-dienoic acid. Bergstrom and Hansson²¹ carried bromination of methyl linoleate with N-bromo succinimide in ultra-violet light and reported the formation of diene conjugation during bromination as a result of the tautomerism of the pentadiene system in a free radical reaction.

PRESENT WORK:

In this laboratory methyl esters of oleic, petroselinic, erucic, stearolic and behenolic acids have been brominated in allylic position with N-bromosuccinimide in presence of benzoyl peroxide as a catalyst. The brominated products were then subjected to thermal dehydrobromination leading to the syntheses of the corresponding conjugated acids, viz., 9:11-octadecadienoic, 6:8-octadecadienoic, 13:15-docosadienoic, 11-octadecen-9-ynoic and 15-docosen-13-ynoic acids, respectively. The production of these acids was confirmed by ozonolysis which gave heptanoic acid in the case of oleic, erucic, stearolic and behenolic acids and decanoic acid in the case of petroselinic acid.

Dehydrobrominated products from the bromo-derivatives of methyl esters of oleic, petroselinic and erucic acids showed blue fluorescence under ultra-violet and had intense absorption maxima at 231 mμ. indicating a diene conjugated system. The values of refractive indices, iodine values, diene values, and catalytic hydrogenation pointed towards the production of conjugated unsaturation and also helped

in the estimation of the extent of unsaturation.

Dehydrobrominated products from the bromo derivatives of methyl esters of stearolic and behenolic acids exhibited ultra-violet absorption maxima at 228 mμ, indicative of a conjugation between an acetylenic and olefinic bond. The presence of acetylenic bond was confirmed by infra-red absorption spectra. All the characteristics of the stearolic acid product, so far determined showed that it may be methyl ester of ximmenynic acid or its isomer.

Allylic bromination of methyl ester of 9:12-linoleic acid with N-bromosuccinimide in presence of benzoyl peroxide and subsequent thermal dehydrobromination yielded a product which showed ultra-violet absorption bands characteristic of diene, triene and tetraene conjugation.

This work was extended to some seed oils (mustard, groundnut, safflower, *Pangomia glabra* (Karanja), *melia indica* (neem), olive, and tobacco oils). In the case of oils, the thermal dehydrobromination was found to lead to gelation. However, the process of dehydrobromination was carried out successfully by the use of pyridine, quinoline, or 2:4:6 collidine. The ultra-violet absorption spectra suggested the presence of both diene and triene conjugation in the component fatty acids of the oil.

EXPERIMENTAL.

All the fatty acids and oils were of high grade purity. The fatty acids were converted to their methyl esters as usual. The experimental details of bromination of methyl oleate and groundnut oil with N-bromosuccinimide and their subsequent dehydrobromination are given below. Similar treatment is applicable to other acids and oils.

Bromination of methyl oleate with equi-molecular proportion of N-bromosuccinimide:

A 400 ml. three-necked flask, equipped with a mercury-sealed stirrer, a condenser with CaCl_2 tube and an inlet for dry nitrogen gas was employed. A solution of methyl oleate (30 g., 0.1 mole) in carbontetrachloride (150 ml.) was placed in the flask and N-bromosuccinimide (18 g., 0.1 mole) and benzoylperoxide (0.6 g.) added to it. The reaction mixture under nitrogen atmosphere was stirred and heated gradually to 70° . After the exothermic reaction subsided, the refluxing was continued for $1\frac{1}{2}$ hrs. The mixture was filtered to remove succinimide and unreacted N-bromosuccinimide, when an orange solution of the brominated product of methyl oleate was obtained.

Thermal dehydrobromination of bromo-derivative of methyl oleate

The above orange solution of bromo-methyl oleate was transferred to another 500 ml. two-necked flask, fitted with a condenser and a CaCl_2 -tube. The flask was heated on a water bath with a continuous current of nitrogen till a test with

ammonia gas indicated that no more HBr fumes were evolved. The solvent was removed under vacuum and the viscous product was dissolved in light petroleum (b.p. 40-60°) and chromatographed over silica gel using ethyl ether as eluant. Characteristics as well as U-V absorption spectrum of the major halogen-free fraction (11.2 g.) were determined as given in Table I and Fig. I.

Similar data of the products obtained from methyl esters of petroselinic, erucic, stearolic and behenolic acids are recorded in Table I and Figs. I and III.

Treatment of methyl oleate with excess of N-bromosuccinimide and subsequent thermal dehydrobromination

A mixture of methyl oleate (30 g., 0.1 mole) N-bromosuccinimide (60 g. 0.3 - 0.4 mole) and benzoyl peroxide (1 g.) in carbon tetrachloride was refluxed for 2 hours at 80-85° under nitrogen atmosphere as above. The orange-coloured liquid was subjected to thermal dehydrobromination. The resultant product (10 g.) after chromatographic purification was found to contain no halogen. The characteristics and U-V absorption curve of the above material and that obtained from methyl ester of erucic acid are recorded in Table I and Fig. II.

Ozonolysis of the dehydrobrominated product from methyl oleate

Ozonised oxygen was passed into a solution of dehydrobrominated product from methyl oleate (20 g.) in anhydrous ethyl acetate (250 ml.) at 0° for 20 hours. The solvent was removed by bubbling dry air through it at about 300 and the ozonide decomposed by treating with water at 60-70°. This was steam distilled and the distillate extracted

with ethyl ether, dried over anhydrous sodium sulphate, removed the solvent and the product redistilled at $125-128^{\circ}/4$ mm. (yield 4.1 g.) (Found: C, 64.3; H, 10.5. Neut.equiv. 130. Calc. for $C_7H_{14}O_2$; C, 64.6; H, 10.8%, Neut.Equiv. 130). Prepared amide in the usual manner, m.p. and mixed m.p.with authentic specimen of heptylic amide $92-94^{\circ}$.

Ozonolysis of dehydrobrominated product from methyl petroselinate

A solution of the dehydrobrominated product from methyl petroselinate (5 g.) in anhydrous ethyl acetate (80 ml.) was ozonised at 0° and the ozonide decomposed with hydrogen peroxide. The product was steam-distilled, and the distillate extracted with ether, dried (Na_2SO_4) removed the solvent and the product redistilled at $135^{\circ}/3-5$ mm. (bath-temp.) yield (1.1 g.) Found, C; 69.6; H, 11.4. Net.Equiv. 170. Calc.for $C_{10}H_{20}O_2$; C, 69.8; H, 11.6% Neut.equiv.172.).

Bromination of groundnut oil with N-bromosuccinimide:

A mixture of groundnut-oil (25 g.), N-bromo succinimide (20 g.) and benzoyl peroxide (0.6 g.) in carbon tetrachloride (175 ml.) was refluxed for $1\frac{1}{2}$ hrs. The reaction product was cooled and succinimide filtered off, giving an orange coloured solution of the brominated groundnut oil.

Dehydrobromination of the above with 2:4:6-collidine:

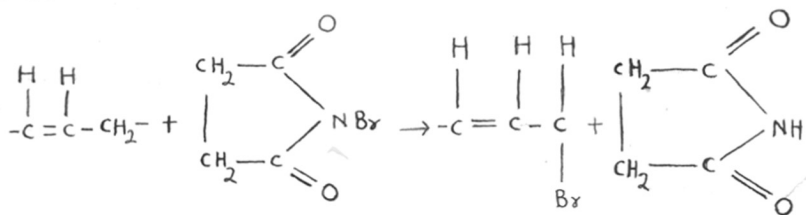
The above product was refluxed with 2:4:6-collidine (125 ml.) for 1 hour. The collidine hydrobromide was filtered off and the filtrate concentrated on water-bath under reduced pressure. The syrupy residue was

taken up in ethyl ether, treated with dil. hydrochloric acid (1:1) and the ethereal layer washed several times successively with water sodium carbonate sol. (1%) and water. It was dried over anhydrous sodium sulphate, the solvent removed in vacuo, giving a dark brown thick liquid. The iodine and diene values of the material are recorded in Table II. A small sample was dissolved in light petroleum (40-60°) and chromatographed over silica gel using ether as eluant. The chromatographed sample was examined for its characteristics and U-V absorption spectrum (Table II and Fig. V). Similar data for the other oils are also recorded.

These products are light brown to reddish brown in colour and exhibit a marked tendency towards polymerisation and gelation.

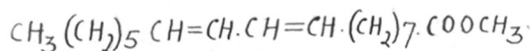
RESULTS AND DISCUSSION.

⁸
Zieler, et al^{15,21} have shown that a hydrogen atom on a methylene group adjacent to an ethylenic double bond may easily be replaced with bromine by means of N-bromosuccinimide. The reaction may be formulated as follows:

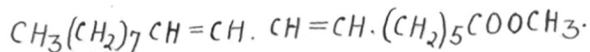
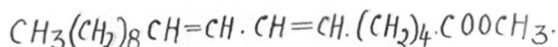


Allylic bromination occurs through a free-radical chain mechanism^{22,23} and the bromo-derivative undergoes a thermal splitting into a molecule of hydrogen bromide and a compound containing a new ethylenic double bond in conjugated position to the olefinic or acetylenic bond initially present in fatty-acids. The free-radical process is favoured in the case of allylic bromination with N-bromosuccinimide because the catalysts like ultra-violet light²⁴ or peroxides²⁵ which are generally believed to catalyse the reactions through free radicals, produce a pronounced effect on the velocity of the reaction.

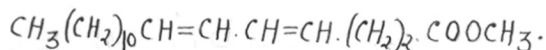
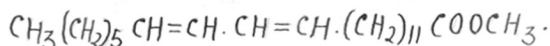
The substitution of hydrogen with bromine may occur on either side of the double bond on using equi-molecular proportions of N-bromosuccinimide and methyl ester of oleic, petroselinic or erucic acid and the resultant products after thermal dehydrobromination may be represented as follows:

Oleic acid

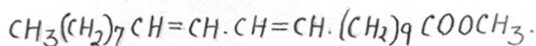
or/and

**Petroselinic acid**

or/and

**Erucic acid**

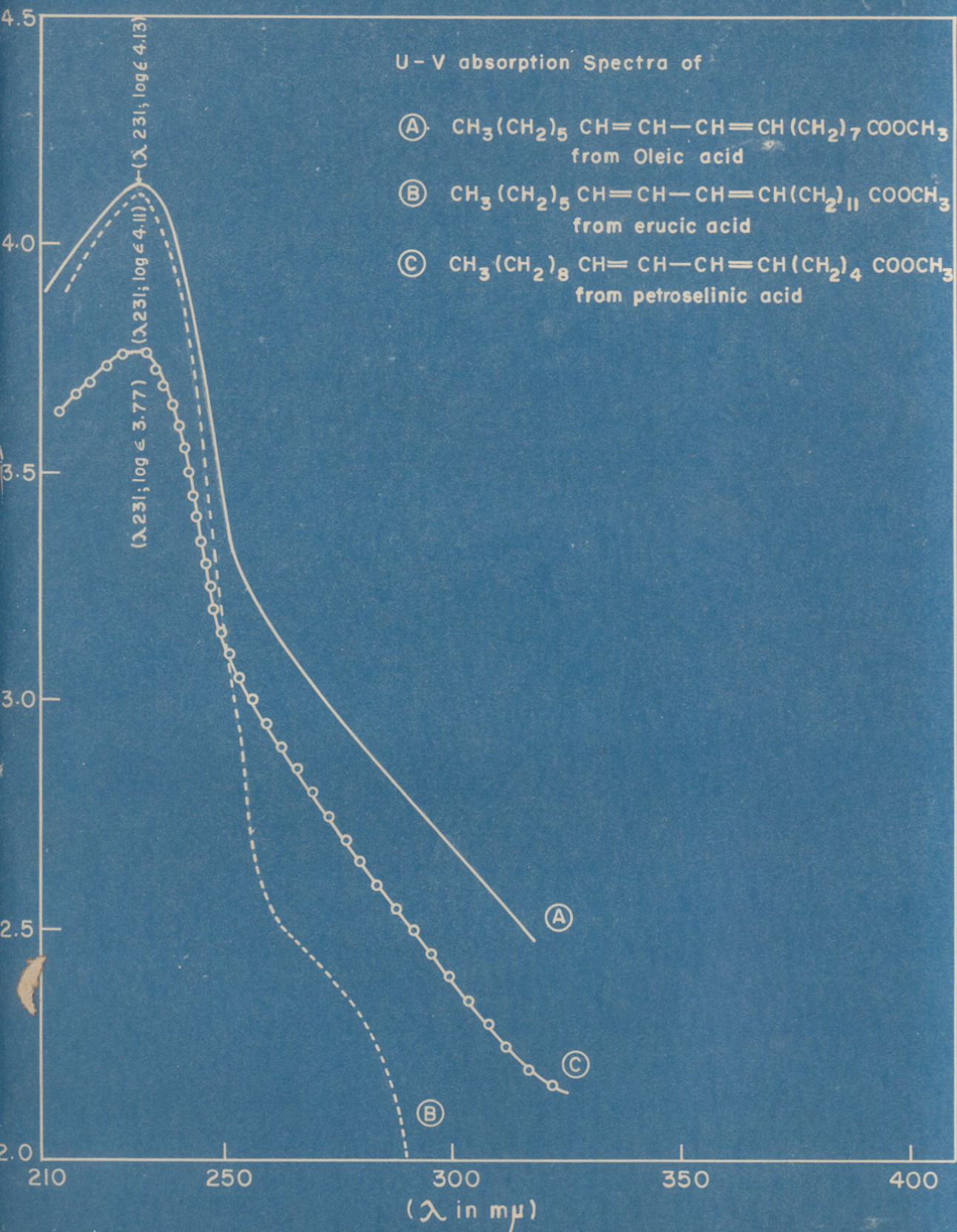
or/and



All these compounds showed blue fluorescence under ultra-violet light and had intense absorption maxima at 231 mμ (Fig. I). This coupled with the increase in iodine values, refractive indices, and diene values (38 to 42) (Table I) of the treated acids clearly show that this method is appreciably effective in creating a double bond in the conjugated position to the initially present one, at least to

Fig. 1

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the extent of 30 to 40%. The materials have been found to polymerise and gel after sometime.

The production of heptanoic acid on ozonisation proved that the thermally dehydrobrominated products from methyl esters of oleic and erucic acids were $\Delta^{9:11}$ -octadecadienoic and $\Delta^{13:15}$ -docosodienoic acids. In the case of methyl petroselinate, $\Delta^{6:8}$ -octadecadienoic acid was formed because ozonisation gave decanoic acid which confirms earlier observation of Clemo and Stevens²⁰. These observations lead to the conclusion that the bromination with N-bromosuccinimide takes place on the allylic CH₂-group farther from the carboxylic group of the acid.

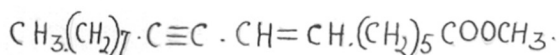
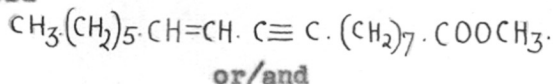
Sutton and Dutta¹⁹ have concluded from allylic bromination of methyl oleate and subsequent oxidation of the brominated products with potassium permanganate that the substitution of bromine takes place on both sides of the double bond and possibly via a route other than a free radical mechanism. In their experiments, they have refluxed a mixture of methyl oleate and N-bromosuccinimide in carbon tetrachloride for four and half hours. It is difficult to compare result obtained in this laboratory. with theirs partly because in this reaction benzoyl peroxide has been used as a catalyst and heated for one and half hours only with an idea that the predominant natural tendency of the primary bromination may be accelerated and partly because attempts have not been made for isolation and purification of the bromo-derivative through distillation and chromatography. However, the observations recorded in this thesis as well as those of Clemo and Stevens²⁰ and

Schmid and Lehman¹⁷ all show that when equi-molecular proportions of N-bromosuccinimide and methyl ester of a mono-olefinic acid are reacted, the tendency of the substitution of bromine is added on the allylic methylene group farther from the carboxylic group through a free radical process.

In the case of oleic and erucic acids when three to four times excess of N-bromosuccinimide was used, a fraction, though in poor yield was obtained through chromatography over silica gel, which exhibited ultra-violet absorption peaks at 231 mμ and 268 mμ (Fig. II) indicating the presence of both diene and triene conjugation. But all attempts to separate the component acids were unsuccessful.

Methyl esters of stearolic and behenolic acids were similarly treated with N-bromosuccinimide in equi-molecular proportions in the presence of benzoyl peroxide catalyst. Their thermally dehydrobrominated products may be formulated as follows:

Stearolic acid



Behenolic acid

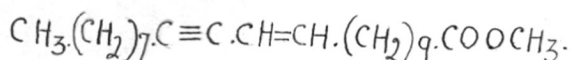
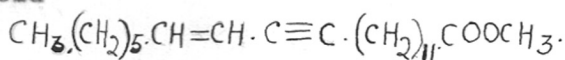
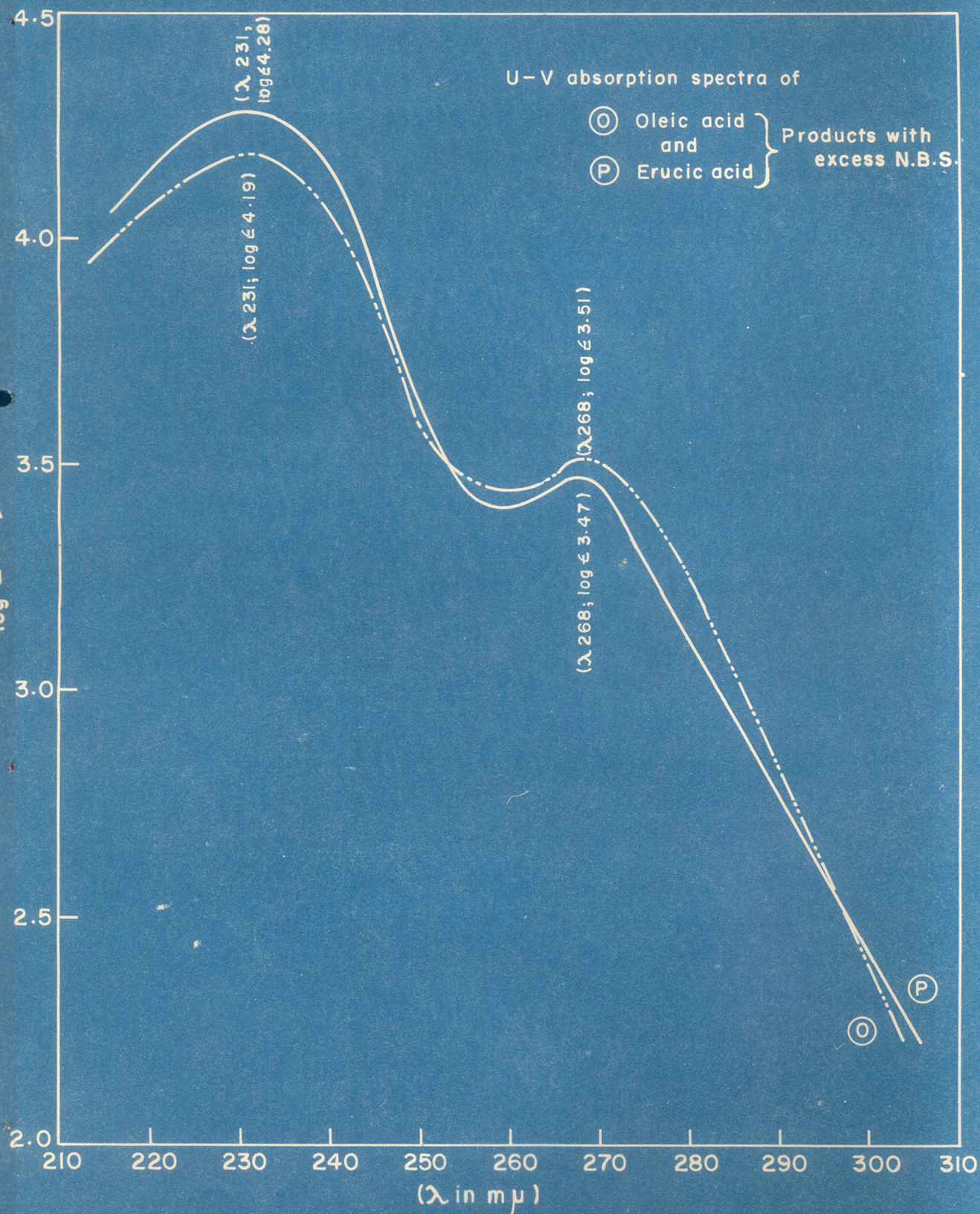


Fig. II

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These materials after chromatographic purification showed light blue fluorescence in ultra-violet and exhibited absorption maxima at 228 mμ (Fig. III) indicative of a conjugation between an acetylenic and olefinic double bond²⁶. The presence of acetylenic bond was confirmed by infra-red absorption spectra²⁷. All the characteristics (Table I) of the stearolic acid product showed that it may be methyl ester of ximenynic acid or its isomer. Ozonisation of the dehydrobrominated products obtained from stearolic and behenolic acids gave heptanoic acid in both the cases showing that they are Δ^{11} -octadecen-9-ynoic and Δ^{15} -docosen-13-ynoic acids respectively. The results of ozonolysis of these conjugated acids indicate that the substitution of bromine in the allylic position generally takes place at a carbon atom further removed from the carboxyl group just as in the case of mono ethenoid acids discussed above.

The results of bromination of methyl ester of $\Delta^{9:12}$ linoleic acid with N-bromosuccinimide in presence of benzoyl peroxide catalyst and subsequent dehydrobromination are also included in Table I. These are similar to those previously reported by Bergstrom and Hansson²⁸. The ultra-violet absorption spectrum (Fig. IV) definitely shows the triene and tetraene conjugation with small amount of diene conjugated product. On account of extra activity of the methylenic group at position 11, the major amount of bromination is expected to take place at this position. In its dehydrobromination together with re-arrangement of double bonds, a triply conjugated system results. Besides

U.-V absorption curves of

(M) $\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}-\text{C}\equiv\text{C}(\text{CH}_2)_7\text{COOCH}_3$
from stearolic acid

(N) $\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}-\text{C}\equiv\text{C}(\text{CH}_2)_{11}\text{COOCH}_3$
from behenolic acid.

(λ 228; $\log \epsilon$ 3.78)

(λ 228; $\log \epsilon$ 3.33)

$\log \epsilon$

(λ in $\text{m}\mu$)

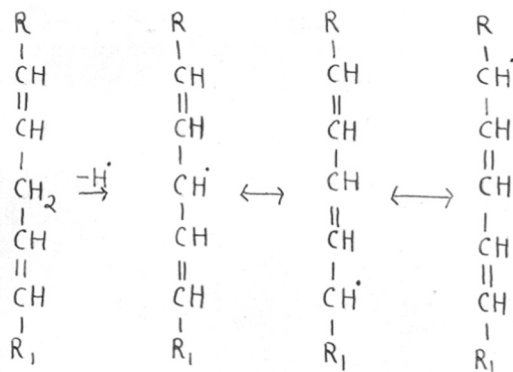
200 210 220 230 240 250 260 270 280 290 300 310 320

(M)

(N)

bromination at the carbon atom at position 11, it may partly also be taking place at the methylene group at position 14. Such a dibromo compound on dehydrobromination will explain the production of tetraene compound. The possible explanation of the presence of a conjugated diene may be merely shifting of the double bonds of the original acid during the process as depicted below:

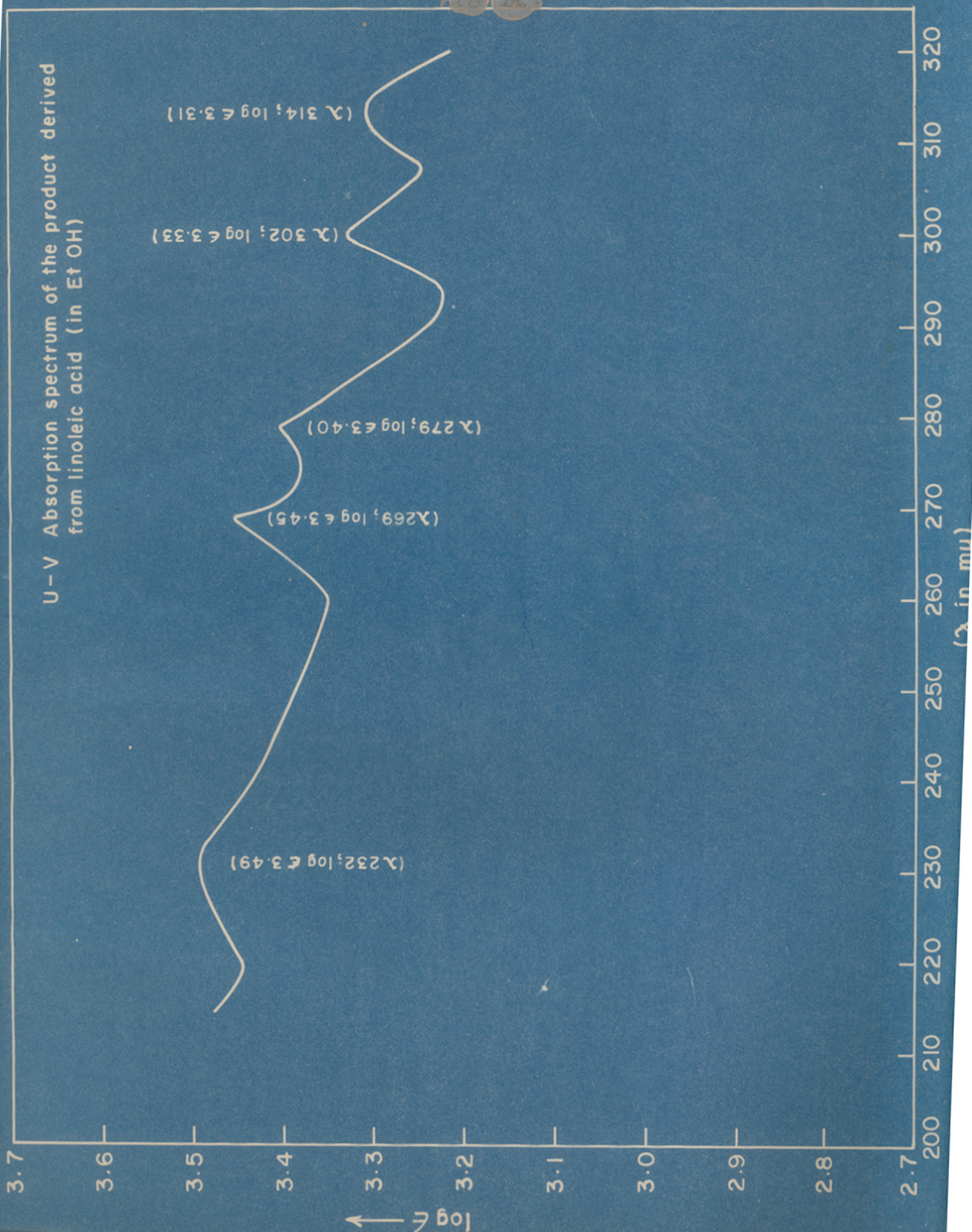
Linoleic acid.



However, no definite compound could be isolated on ozonization of the dehydrobrominated product.

When the above process of inducing conjugation was applied to various oils it was found that complete dehydrobromination could only be effected by the use of 2:4:6-collidine, pyridine or quinoline. Some characteristics of these products before and after chromatographic treatment over silica gel and those of the original oils are recorded in (Table II). Their u.v.

U-V Absorption spectrum of the product derived from linoleic acid (in Et OH)



absorption spectra (Fig. V) and values (Table III) show the presence of both diene and triene conjugation in the component fatty acids. Due to the higher amounts of linoleic acid (66-70%) in tobacco and safflower seed oils the triene conjugated component acids were found to be much higher than in other oils so much so that these products gelled shortly after they were prepared. Their films set to the wrinkled patterns as is usually the case with conjugated oils of tung and kamala type. Even other products exhibited tendency towards polymerisation. Their dark brown colour became lighter by chromatographic purification. They also showed greenish-blue fluorescence in ultra-violet light.

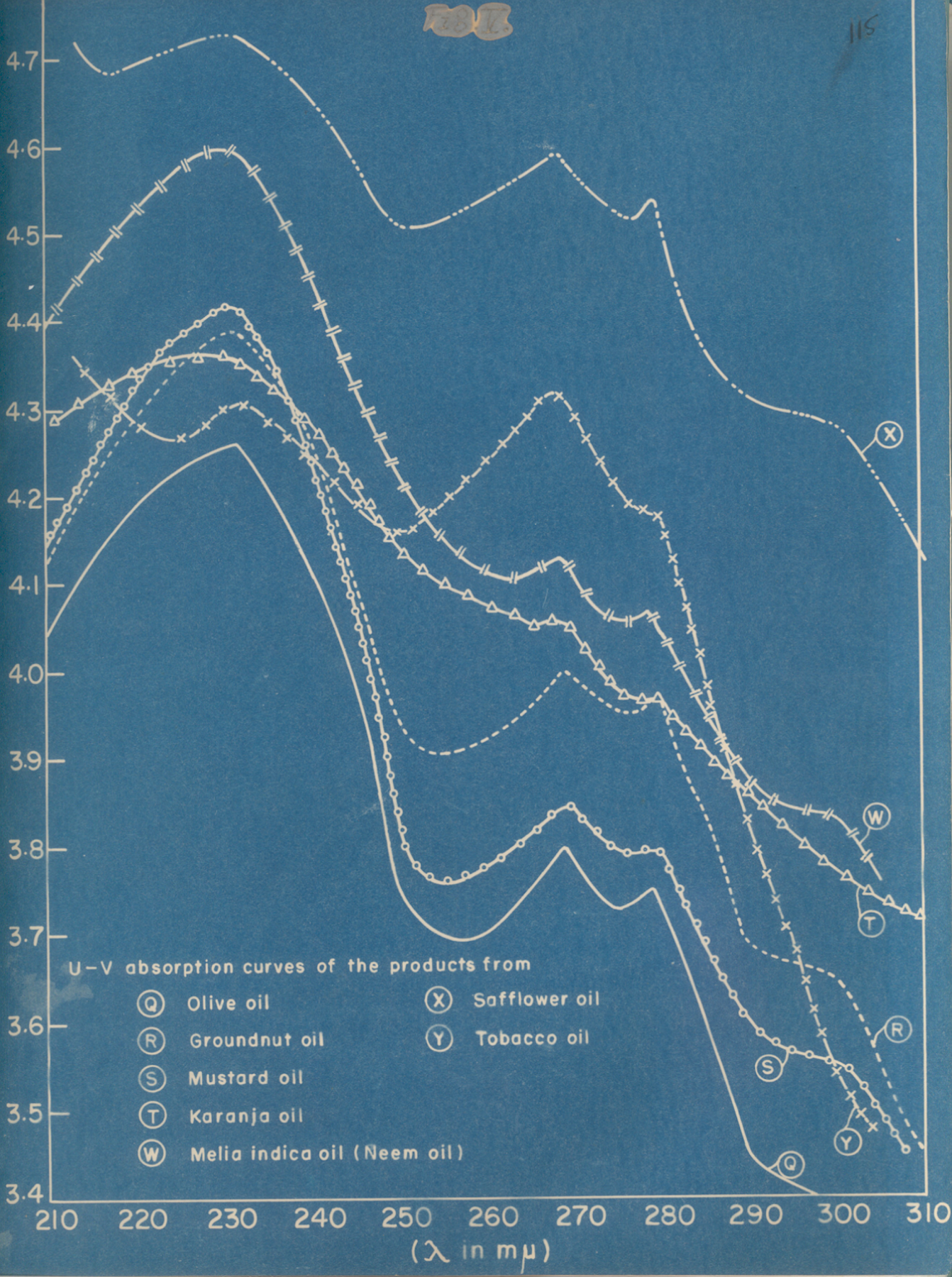


TABLE I.

Characteristics of various unsaturated fatty-acids before and after treatment with N-bromosuccinimide.

Methyl ester of fatty acid	Original		After treatment with N-bromo-succinimide		
	I.V. (R & K) (29)	n_D^{500}	I.V. (R & K) (29)	n_D^{500}	Diene value (30)
Erucic	74.5	1.4475	96.0	1.4690	38.4
Oleic	89.8	1.4420	128.0	1.4640	42.8
Petroselinic	89.9	1.4421	121.4	1.4682	39.7
Stearolic	85.1	1.4452	123.4	1.4772	36.2
Behenolic	70.5	1.4582	109.3	1.4722	37.3
Linoleic	180.4	1.4530	247.3	1.4725	67.5

N.B: The diene value is expressed in terms of the equivalent number of centigrams of iodine per gram of the sample.

TABLE II.

Characteristics of fatty oils. Characteristics of oils before and after treatment with N-bromosuccinimide.

Vegetable oils.	Original		After treatment with N-bromo succinimide before chromatography		After treatment with N-bromo succinimide after chromatography	
	I.V. (R & K)	n _D ⁶⁰	I.V. (R & K) 29	Diene value 30	I.V. 29 (R & K)	n _D ⁶⁰ Diene value 30
Mustard	96.0	1.4614	115.5	21.9	122.4	1.4860 28.4
Groundnut	93.2	1.4592	113.2	33.0	123.1	1.4850 33.1
Olive	83.6	1.4590	106.3	23.7	105.9	1.4643 28.3
Tobacco seed	138.6	1.4651	150.9	26.3	155.4 (The treated oil partly gelled).	1.4880 34.8
Safflower seed	139.6	1.4622	146.3	20.9	148.6 (The treated oil partly gelled).	1.4873 25.8
Pongamia glabra (Karanja)	81.5	1.4630	113.5	25.6	125.4	1.4738 30.3
Melia indica (Neem)	81.9	1.4572	101.7	20.7	108.1	1.4643 27.1

TABLE III.

U.V. Values of the treated oils in n-hexane.

Oil	Curve reference in Fig. V	Wave length ()	log	Inference
Olive	Q	232	4.26	Diene
		269	3.80)	Triene
		279	3.75)	
Groundnut oil	R	232	4.39	Diene
		269	4.0)	Triene
		280	3.97)	
Mustard oil	S	232	4.42	Diene
		269	3.85)	Triene
		280	3.80)	
Pongamia glabra (Karanja oil)	T	231	4.36	Diene
		269	4.06)	Triene
		279	3.97)	
Melia indica (neem oil)	W	231	4.60	Diene
		269	4.13)	Triene
		279	4.07)	
Safflower seed oil	X	232	4.73	Diene
		269	4.59)	Triene
		280	4.54)	
Tobacco seed oil	Y	232	4.31	Diene
		268	4.32)	Triene
		279	4.19)	

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