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United Nations Industrial Development Organization

Expert group meeting on pre-investment
considerations and technical and economic
production criteria in the oilseed processing industry
Vienna, Austria 16 - 20 October 1972

HYDROGENATION OF VEGETABLE OILS AND VEGETABLE GHEE PRODUCTION[1]

by

H.B.W. Patterson
Technical Officer
Unilever Limited
London, England

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SUMMARY

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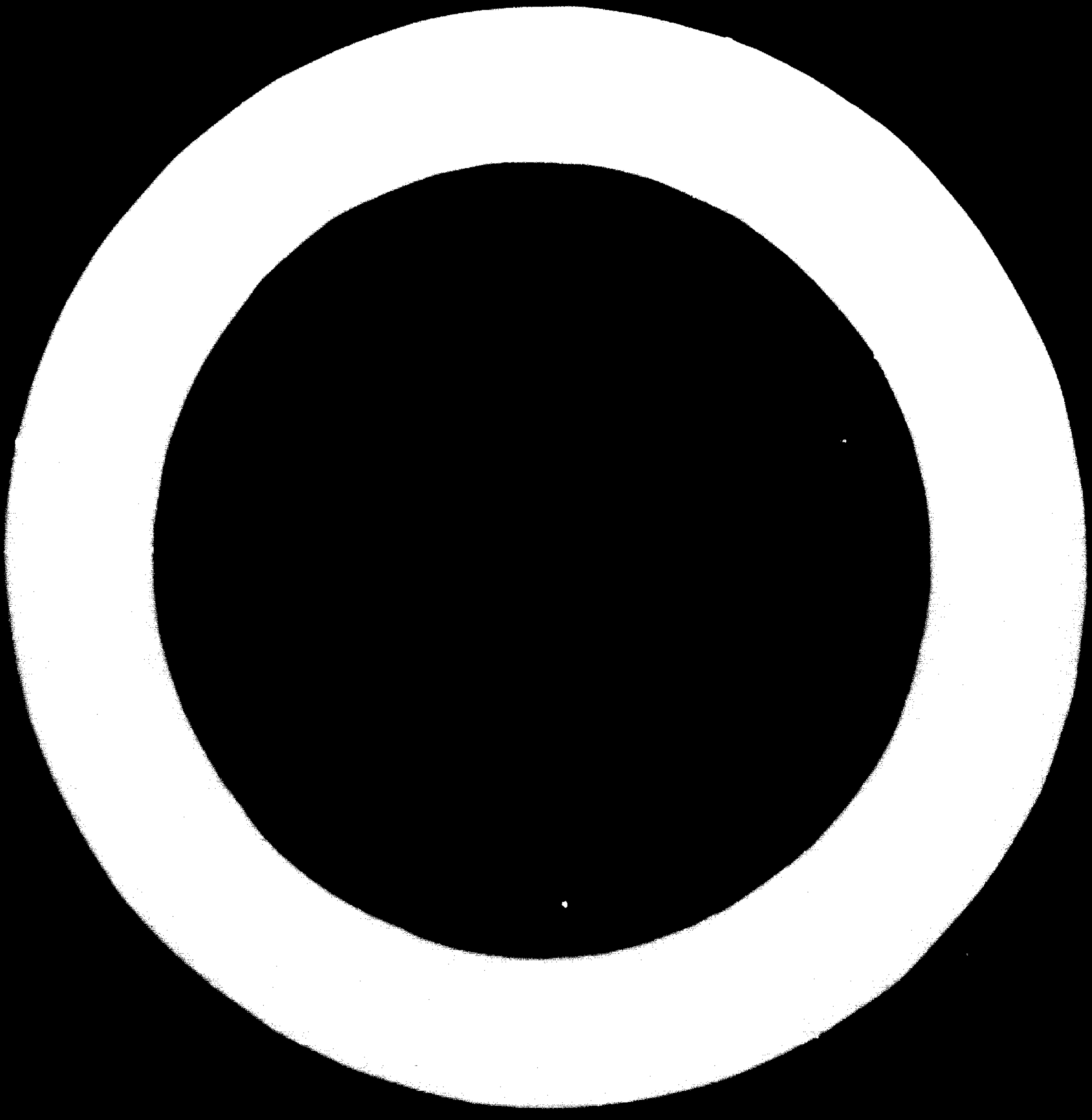
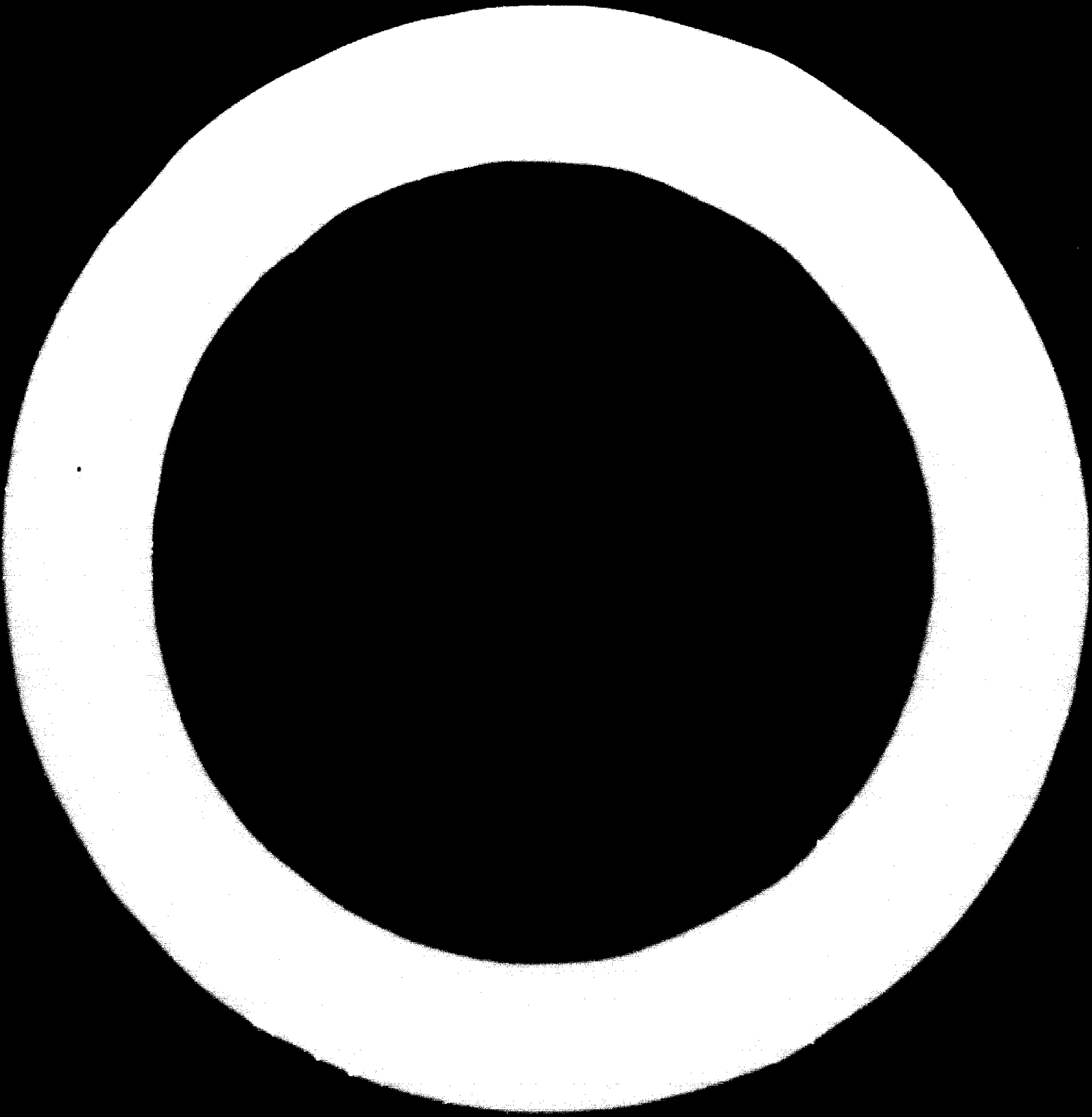




SUMMARY

HYDROGENATION OF VEGETABLE OILS

and

VEGETABLE GHEE PRODUCTION

Oils and fats consist of mixtures of triglycerides which themselves differ from one another by reason of the different fatty acid groups they contain. By combining hydrogen with those fatty acids which do not already contain their full complement the liquid oil is progressively converted to a solid fat. Colour and odour decrease greatly; the fat becomes increasingly resistant to oxidation. At the same time other structural changes known as isomerization occur which can affect the texture and flavour stability of the oil.

Hydrogenation depends upon the intimate mixing of oil and hydrogen in the presence of a catalyst. Temperature, pressure, mixing efficiency, type and amount of catalyst all affect the rate at which the reaction proceeds and what subsidiary effects arise.

Before hydrogenation, oils should be freed from impurities, especially those which poison the catalyst. This refining is commonly performed with the help of aqueous alkali but organic solvents or steam stripping at much reduced pressure are sometimes employed. Earth bleaching is also part of the preliminary treatment. A post refining is performed on the hydrogenated oil to render it completely bland.

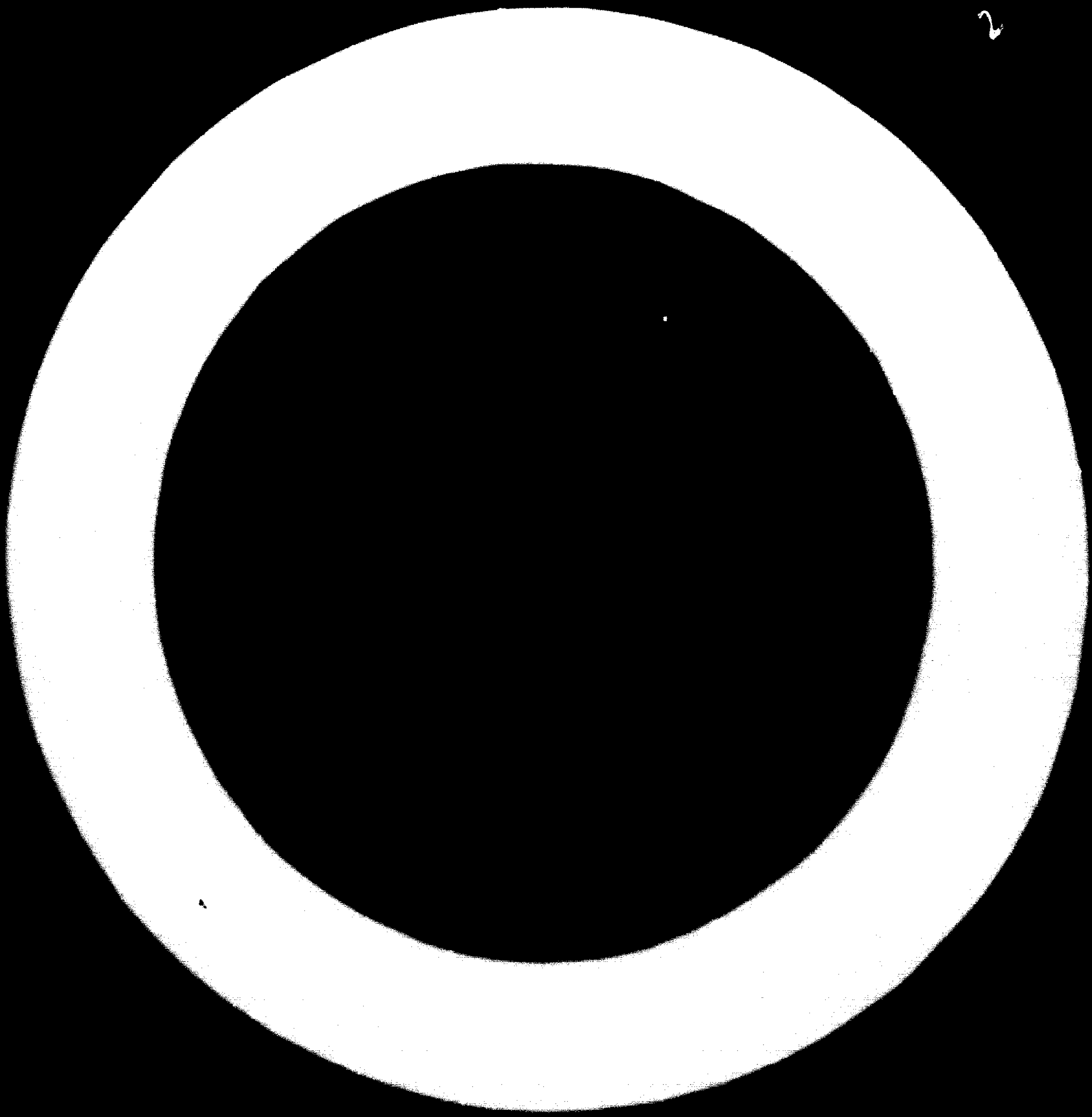
Since, within wide proportions, mixtures of hydrogen and air will explode if ignited, stringent precautions must be observed in all parts of the process to prevent these mixtures from forming and to prevent their ignition.

Although several metals can act as catalysts in promoting the combination of oil and hydrogen nickel dominates the field because of its efficiency and acceptable cost. The condition of the finely divided nickel surface plays a major part in determining whether the hydrogenation is selective or not. Selectivity means the preferential partial hydrogenation of those fatty acid groups which are most deficient in hydrogen. Isomerization accompanies selective hydrogenation; texture and stability of the product are intimately affected. Since vegetable oils in many cases contain little catalyst poison good economy in the repeated use of catalyst is often possible.

Hydrogen is currently produced either from hydrocarbons, including natural gas, by the reforming process, or effectively by the elctrolysis of water. A minimum hydrogen purity of 99.5% is obtained. This high purity facilitates the progress of the hydrogenation reaction and the design of the plant in which it is performed. Choice of method of hydrogen production depends upon costs of hydrocarbon, electricity and scale of production. Large plants tend to use hydrocarbon reforming as the cheapest method; sometimes by-product hydrogen is available from a large electrolytic plant. Smaller plants may be well suited by their own electrolytic production of hydrogen especially if this is linked with ease of maintenance and sale of by-product oxygen.

Vegetable ghee production depends upon the hydrogenation of one or more vegetable oils. The final product may include a proportion of unhydrogenated vegetable oil. The aim is to produce a nutritious fat whose somewhat extended melting range is at least equal to that of ghee itself and whose stability is assured in arduous and prolonged storage conditions.

Vitamin is usually added; colouring and flavour depend upon local legislation and preference.



CONTENTS

THE HYDROGENATION PROCESS

BASIC CHEMISTRY

Oils and Fats are the popular terms for what chemists describe as triglycerides. If the ambient temperature is such that the material is liquid it is called an oil and if solid a fat. Indeed the liquids known in the tropics as coconut and palm kernel oils were at one time often referred to as fats in temperate regions. Triglyceride molecules are the result of the combination of three molecules of fatty acid with one of glycerol. In the appropriate chemical plant triglycerides can easily be reacted with excess glycerol to form mono and diglycerides which have their own special uses as emulsifiers for example, but we are not here concerned with these. A whole series of related fatty acids exists and when more than one member of the series is represented among the three fatty acids of a triglyceride the resultant compound is called a mixed triglyceride.

Triglyceride

fatty acid (1)
Glycerol " " (2)
" " (3)

1 = 2 = 3 = simple triglyceride
all others = mixed "

Natural oils and fats are physical mixtures of several triglycerides which themselves are mainly mixed triglycerides. Naturally the character of a fat will depend upon the relative amounts of different triglycerides it contains, just as the character of any individual triglyceride depends in turn upon the proportions it contains of different fatty acid groups. Hydrogenation is concerned with altering the properties of individual constituent fatty acid groups and hence through them the properties and behaviour of the fat as a whole.

Fatty acids consist of a chain of carbon atoms linked to one another and also combined with hydrogen atoms. One end of the chain terminates in a H_3C- (methyl) group and the other with a -COOH (carboxyl) group thus:-

Fatty acid

$$H_3C.CH_2.CH_2 \text{ ------ } CH_2.CH_2.COOH$$

It is the carboxyl group which links with the glycerol to form a glyceride. In vegetable oils we are concerned with fatty acids which contain from 6 to 24 carbon atoms in the chain, the most important members being those with 16 and 18 carbon atoms. Fatty acids with an even number of carbon atoms constitute the vast majority of the fatty acids found in the natural oils and fats.

2. UNSATURATION AND CHAIN LENGTH

It happens frequently that two neighbouring carbon atoms are each without one of their usual two hydrogen atoms and are linked with one another via a double bond thus,

---$CH_2.CH{:}CH.CH_2$---

Because it lacks its full complement of hydrogen the chain is then described as unsaturated. Fatty acids containing two or more double bonds are known as polyunsaturated fatty acids. Where the two missing hydrogen atoms each lie to the same side of the chain (cis) the double bond is seen as part of a rigid arc in the length of the chain; where the missing neighbouring hydrogen atoms lie across (trans) the length of the chain towards opposite sides, no such arc is represented. Whereas there is complete free rotation of the atoms joined by a single bond, the double bond makes possible only the two fixed positions, cis and trans, whilst there is no flexibility at all in the arrangement involving a triple bond. The cis arrangement greatly predominates in the natural fatty acids which contain double bonds; it is associated with a liquid or lower melting condition, greater solubility and chemical reactivity. By contrast saturated fatty acids are associated with solid or higher melting characteristics. When double and single bonds alternate in a chain a conjugated system exists; this is notably reactive and to that extent unstable. When two double bonds are separated by a $.CH_2.$ group the resultant arrangement, referred to as a skipped arrangement, is still quite chemically reactive and this is the usual spacing in nature. Such a $.CH_2.$ group is known as an active methylene group.

$---CH_2.CH{:}CH.CH{:}CH.CH_2---$ conjugated

$---CH_2.CH{:}CH.CH_2.CH{:}CH.CH_2---$ skipped

$CH_3---(.CH_2.CH{:}CH.)_n---COO.$

frequent arrangement in nature, cis predominating.

Although the presence of one or more double bonds has a major influence on the character a fatty acid of a certain chain length (number of carbon atoms) it must also be stated here that the length of chain itself is quite an important factor, the shorter the chain the lower the melting point, the greater the solubility, when comparing fatty acids of an even number of carbon atoms with one another, and likewise for the odd series.

3. ORIGINS OF INDUSTRIAL HYDROGENATION OF FATTY OILS

When there was a shortage of fats in Europe of sufficiently firm texture for margarine manufacture the classic researches of Sabatier and Senderens were turned to practical account in 1906 by Normann who supervised the erection and commissioning of the first industrial plant for the hydrogenation of liquid oils to produce fats at Warrington, U.K. The oil hydrogenation industry grew rapidly to become within ten years - and still remains - the major route for chemical modification of oils and fats so that one oil could take the place of another when economically desirable. Eventually, modified varieties were produced with enhanced characteristics from the consumer's point of view. In 1913 Norwegian and German scientists demonstrated the feasibility of using hydrogenated marine oil for edible purposes. The use of hydrogenated oil for soapmaking, and in particular the substitution of hydrogenated whale oil for tallow, had already been established.

Today the three major oil modification techniques of hydrogenation, fractionation and interesterification may all be employed in varying sequence for the production of specialised and sophisticated products.

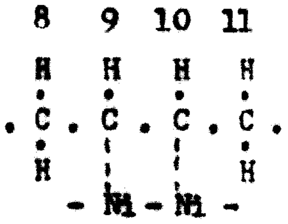
4. MAIN EFFECTS OF HYDROGENATION

The major effect of hydrogenation is to add hydrogen to the unsaturated fatty acids with the help of a finely divided metal such as nickel acting as a catalyst. Thus as the double bonds are saturated and therefore progressively disappear a higher melting material is formed, that is, the oil is transformed to a fat. Several side effects occur and, so to speak, provide a bonus. The characteristic odour and flavour of the raw oils disappear, although for edible purposes this effect must be completed by deodorisation as for any other oil. Since double bonds are the focal points of chemical activity and provide the starting point for the attack of atmospheric oxygen which leads first to flavour reversion and finally rancidity of the fat it is not at all surprising that reducing the number of double bonds makes the oil or fat more secure against subsequent oxidation. Keepability or shelf life improves very noticeably. Carotene, chlorophyll and other pigment substances which gave the raw oil its yellow or reddish appearance are altered during hydrogenation so that they either disappear altogether or the oil remains a pale yellow.

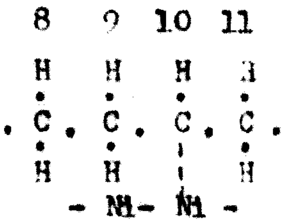
5. ISOMERIZATION

There are other important reactions which occur to a lesser or greater extent according to conditions whilst the main hydrogenation is in process. Put simply when a carbon - carbon double bond presents itself at the nickel catalyst surface the distance between two adjacent active nickel atoms and between the two carbon atoms is very similar, so that each carbon atom is able to form some kind of link with one of the adjacent nickel atoms. It is the polyunsaturated fatty acids which are most readily adsorbed.

Hydrogen, meanwhile, is being dispersed into the oil and also concentrates at the nickel surface. In this situation it is very much easier for the hydrogen to combine with the unsaturated carbon atoms of the double bond than if no catalyst were available. If both carbons acquire a hydrogen the double bond is reduced to a single bond and the molecule is desorbed from the active site.



(a)



(b)

It may happen that when the double bond is adsorbed, (a), no. 9 C atom acquires hydrogen first, (b). Then before no. 10 C atom gains a hydrogen, a hydrogen atom is lost from either no. 9 or no. 11 C atom and a double bond reforms either on the original 9 - 10 site or at the 10 - 11 site. If the latter happens the double bond has migrated and this indeed may be so repeatedly during the period an oil is being hydrogenated. Hence positional isomers are formed. Further, depending upon which of the two hydrogen atoms on no. 9 C is lost the double bond reforms in the cis or trans configuration. The same holds good as regards no. 11 C atom. The change from cis to trans (or vice versa) is a geometric isomerism since it is seen as a change in molecular shape. The above is one of the more commonly accepted explanations of how these very important side reactions take place. Since change from cis to trans itself is a move towards the higher melting and even solid condition it is evident that the texture of the end product will be markedly affected depending upon whether it contains a high proportion of trans or cis double bonds, apart from the question of how many double bonds may have disappeared. A high proportion - say two thirds - of the double bonds in the trans form will indicate a high amount of moderately low melting solids so that the product is very firm at 20°C, much less so at 30°C and perhaps completely liquid at 37°C. If the percentage solid fat content at different temperatures is drawn on a graph the curve will be seen to descend steeply as the temperature becomes greater.

This effect is sometimes sought in hydrogenation and is encouraged by low dispersion of the hydrogen brought about by decreased agitation, operating pressures from 0.3 to 1.0 atmos. for example and operating temperatures preferably above 160°C. All of which factors tend to keep the concentration or availability of hydrogen at the nickel surface rather low. A partly poisoned or considerably exhausted nickel catalyst will promote the above kinds of isomerization. Conversely lower operating temperatures (150°C or less), fresh active nickel and very good hydrogen dispersion tend to suppress isomerization and this effect is also sometimes required for particular hardened oils which soften more gradually before finally melting.

6. SOLID FAT CONTENT AND TEXTURE

One technique of estimating the proportion of solid fat in what is truly a mixture of solid and liquid is known as dilatometry. In common with most other substances oils tend to expand on heating, or contract on cooling by a specific amount which can be determined. If the temperature of a convenient weight of fat is raised steadily by 5°C or 10°C intervals and the volume carefully noted after due pause at each step then any increase over and above normal thermal expansion is due to a change of solid phase to liquid. If this volume is expressed in cubic millimetres and related to 25 grms. then the dilatation value is a measure of the difference in volume actually occupied by the fat and what it would occupy if it were entirely liquid at that temperature. If the difference is large the proportion of solid is high and the dilatation value is high; conversely a low dilatation value indicates a low amount of solid. Completely solid, the fat will have a dilatation of ca 2500; at the slip melting point the value is ca 100. Frequently the value is expressed in relation to

1 grm. and is known as the solid fat index, (SFI) since a completely solid fat will have an SFI of 100; at the slip m.p. the SFI is found to be ca 4. The procedure is empiric, rests on certain assumptions and must always be followed rigorously if the results are to be dependable. Low resolution nuclear magnetic resonance is gaining in popularity as another means of estimating percentage solid fat content, (SFC).

From what has just been said it will be evident that the melting point (however it may be determined) is only a very limited indication of the texture of a fat since natural fats are in fact a mixture of glycerides which each have their own individual melting points. Information on the solid content over a wide range of temperatures from 0°C or 20°C upwards is needed.

7. SIDE EFFECTS

Polyunsaturated fatty acids groups, especially those with three or more double bonds such as linolenic and higher unsaturated fatty acids, tend to form a small proportion of cyclic aromatic fatty acids if at the outset they are hydrogenated in conditions of hydrogen scarcity, and comparatively high temperatures (e.g. 200°C). This undesirable tendency is kept safely under control by operating at a moderately low temperature of 150°C or lower and with good hydrogen dispersion in the early part of the hydrogenation until the most unsaturated fatty acids have been at least partly hydrogenated. Polycyclic aromatic hydro-carbons already present in some vegetable oils such as coconut and sunflower to the maximum of 3 mg/Kg. can be removed by certain active carbons added along with the bleaching earth during the refining of the unhardened oil. Apparently whilst deodorisation is capable of removing hydrocarbons of a four ring structure it does not have the same capability as regards five ring structures, hence the appropriate absorbent carbon is employed.

8. SELECTIVITY

This brings us finally to the very important concept of selectivity in hydrogenation. It has already been mentioned above that the polyunsaturated fatty acid groups are more readily absorbed onto the active sites of the nickel catalyst surface. When the overall hydrogenation effect is such that fatty acid groups with three double bonds are nearly all reduced to two double bonds before those with two are reduced to one, or when those with two are nearly all reduced to one, before the mono-unsaturated groups are hardened to fully saturated, then conditions of good or high selectivity exists. There is, so to speak, a progressive orderly diminution of the most unsaturated groups. If many saturated groups are produced in advance of the reduction of the polyunsaturated to less unsaturated ones the selectivity is poor or non-existent. Closely associated with this concept of selectivity is the parallel one that only one fatty acid group of a triglyceride experiences hydrogenation during one period of proximity to the entire catalyst surface. If this condition does not exist the chances are greater, as hardening continues, of producing more fully saturated high melting triglycerides than would be the case if hardening of the various unsaturated triglycerides present were on a truly random basis. Selectivity is favoured by having only a moderate concentration of hydrogen on the catalyst surface, that is, medium to high temperatures (160° - 200°C), increased nickel surface, low stirring rate, lower pressures of about 0.5 to 1.0 atmospheres. The importance of the type of catalyst surface in selectivity is considered in Chap. III.

It is now obvious that those operating conditions which favour selectivity also favour isomerization. On the occasions when the hardener is not particularly concerned to obtain either effect his task is very straight forward - normal agitation, pressures about 3 atmos. and a wide choice of temperatures up to 200°C. If selectivity is wanted with a minimum of isomerization a compromise in operating conditions such as temperature and pressure has to be accepted and it becomes particularly important to employ a fresh catalyst which is known to promote selective hydrogenation.

Table 1

Fatty acid type percentage composition of vegetable oils *

		carb atoms : double bonds						
Oil	I.V.	16:0.	16:1.	18:0.	18:1.	18:2.	18:3.	Others
Coconut	10	9	-	2.5	7	2.5	-	8:0 (8%), 10:0 (6%), 12:0 (47%), 14:0 (18%)
Palm kernel	16	8	-	2.5	14	2.5	-	8:0 (6%), 10:0 (4%), 12:0 (47%), 14:0 (16%)
Palm (Ng.)	57	40	T	5	40.5	12	T	14:0 (1%), 20:0 (T).
Olive	85	11.5	1.5	2	74	9	1.5	20:0 (T)
Groundnut (Ng.)	88	10	-	3.5	59	20	T	20:0 (1.5%) 20:1 (1.5%), 22:0 (2.5%), 24:0 (1.5%)
Cotton	107	25	T	2.5	18	52	T	14:0 (1%), 20:0 (T).
Sunflower	132	6.5	T	5	23	63	T	20:0, 20:1, 20:2, - all (T).
Soyabean	137	10	T	3.5	21	56	8	20:0, 20:1 - both (T).

T = 0.5% or less

C12:0 laurie,

C16:0 palmitic

C18:0 stearic, C18:1 oleic, C18:2 linoleic, C18:3 linolenic.

9. TYPICAL COMPOSITION OF VEGETABLE OILS

Table 1 shows the typical distribution of saturated, monounsaturated and polyunsaturated fatty acids of several vegetable oils. In the case of some species there is appreciable variation in the total degree of unsaturation - as seen by Iodine Value (I.V.) - and the relative proportions of mono unsats. and poly unsats. These variations relate both to genetic strains and regional climatic differences.

10. LAURIC OILS

The first two oils, coconut and palm kernel contain already in the crude state over 50% sats. and so it is not altogether surprising they are solid in temperate climates. When fully hydrogenated, coconut oil has a slip melting point of 33°C and palm kernel 39°C. The high proportion of short chain (C8 to C12) fatty acids and the general triglyceride make up contribute to the fact that these oils possess a steep dilatation curve even before hardening and very obviously so afterwards. Their low unsaturation means they are resistant to oxidation. If a little free fatty acid or monoglyceride does form by hydrolytic splitting of the triglycerides the off-flavour is obvious. Apart from use as cooking oil in the tropical regions of their origin the quick melting effect of the lauric and hardened lauric oils (babassu and tucum included) has led in temperate climates to their wide use in confectionery and margarines. Whereas at one time they provided a major component of many margarine blends in Europe and U.S.A. their use has declined during the past forty years because of their expense and their replacement by other oils, especially as the technique of hydrogenation advanced.

11. PALM OIL

Palm oil with slightly less than 50% sats. melts at 34° - 36°C and by the time its I.V. has been dropped only 8 points by hydrogenation quite a firm fat results of 42° - 44°C m.p. When fully hardened a 58°C m.p. is obtained. The texture or melting behaviour of palm oil itself is well known to be particularly related to certain specific triglycerides such as oleo-dipalmitin which it contains. The more saturated and hence higher melting triglycerides may be separated by a variety of chilling techniques and the more liquid fraction partly hydrogenated separately so as to prepare a product melting more sharply. The continued improvement in the quality of crude palm oil and the yield from cultivation encourages its greater employment in margarine and cooking fats.

12. OLIVE, GROUNDNUT AND COTTONSEED OILS

Olive oil is prized as salad and cooking oil so there has been no widespread incentive to hydrogenate it. The very high proportion of mono-unsat. (C18:1, oleic, 74%) is the basis of its stability.

Groundnut oil is an excellent all-purpose oil. Both saturated fatty acids (SAFA) and polyunsaturated fatty acids (PUFA) are moderately low, the latter being in the valuable form of essential fatty acid (EFA),(see para 49). As well as being used for cooking, frying and in margarine blends groundnut oil forms a soft solid of around 30°C m.p. when its I.V. is dropped to about 72 and when fully hardened reaches 62°C m.p. Short and long melting ranges ("steep" and "flat" dilatation curves) are obtainable by variation of hardening conditions. If the crude oil has suffered oxidative damage the fully refined medium hardened oil may show a waxy taste.

Although cotton oil shows a considerable increase in PUFA (52%) over groundnut it is still quite feasible to use it in frying; it may be used as a liquid component in margarine. Hydrogenation to 80 I.V. produces fat in the melting range 30° - 34°C. Both steep and flat dilatation curves are obtainable and this has extended its use in margarine and vegetable shortenings.

For many years in countries where it is readily available cottonseed oil has been hydrogenated to form the basis of vegetable ghee (Chap. V). Fully hardened the m.p. is 62°C. Up to about 5% fully hardened groundnut or cottonseed has been commonly employed in compound shortenings to extend the plastic range of the blend by lifting the dilatation (D) or (SFI) at 30°C and 40°C, hence achieving a slip m.p. of around 42°C.

13. SUNFLOWER OIL, SOYABEAN OIL

Sunflower is rich in the form of linoleic acid (C18:2) which is an important EFA and from which the body can synthesise its very important arachidonic acid. Thus sunflower oil is widely sought as a liquid component of margarine and included at a high level in special dietary margarines. It has also been hydrogenated, especially in countries having ready access to plentiful supplies and is used in this way, for example, in Turkey in the production of vegetable ghee. Related to the high proportion of fatty acid groups of the same chain length (C18, ca 91%) there is a tendency for the hardened fat to change its crystalline form over a period of time and produce "graininess" or "sandiness" in the product. One method of controlling this has been to ensure that the blend contains an amount of other vegetable oil(s) which reduces this marked preponderance of the C18. Hydrogenation to 84 I.V. gives a 32°C m.p. and when fully hardened a 68°C slip m.p. is reached.

Lastly in the vegetable oils here chosen for review there comes soyabean oil which has advanced in quality, cultivation and processing since the 1930's, to become the world's no. 1 oil crop, although the value of the meal is at least equally responsible for this growth. SAFA content (ca 10%) is relatively low; the linolenic acid is a source of sensitivity to attack by atmospheric oxygen leading to flavour reversion and, in the limit, rancidity.

Linolenic acid (C18:3) is not the only source of off flavour development and indeed it is unnecessary to remove all the linolenic group by hydrogenating to linoleic or further in order to enhance stability. Lightly hydrogenated soyabean oils still containing one or two percent linolenic have good keepability. Indeed, careful extraction of undamaged beans followed by degumming and alkaline refining preferably out of contact with air produces after deodorisation an excellent bland product which is commonly used as a liquid oil component of margarine. The lightly hydrogenated oil is fractionated in the U.S.A. to remove the small percentage of higher melting triglycerides; after deodorisation a liquid salad oil of enhanced quality and stability is obtained. Large tonnages of soyabean oil are now hydrogenated and employed (along with other hydrogenated vegetable oils) in the manufacture of vegetable ghee.

The linoleic acid is present in the most active [illegible] A form. Inevitably a proportion of this is lost whilst hydrogenating linolenic groups because of the very limited selectivity of nickel catalyst in favouring the conversion of C18:3 to C18:2 at the expense of all other reactions: copper is superior in this respect. The linolenic acid group when hydrogenated is prone to produce a proportion of isomeric linoleic groups which on being oxidised may, in their turn, give rise to small amounts of trans 6-nonenal. The latter is an aldehyde identified as the source of the so-called linolenic hardening flavour.

When the I.V. of soyabean oil has been reduced by hydrogenation to about 100 a soft solid with a slip melting point below 30°C is obtained. The fully hardened oil melts at 68°C.

14. HYDROGEN REQUIREMENTS

From the above descriptions it is possible to see the very wide variety of hydrogenated products which may be derived from vegetable oils. Flavour stability is always required; the texture or melting behaviour relates to the intended use. Since the unsaturation is spoken of in terms of iodine value it will be useful to remember that to reduce the iodine value of 1000 Kg., (2205 lbs.) of oil by one unit the volume of pure dry hydrogen taken up is 0.9319 cub. metres measured at 15°C and 760 mm., (32.9 cu. ft). Since a certain amount of hydrogen is lost in compressing, purging etc. this may be conveniently rounded off for large scale practical purposes to 1 cub. metre per metric tonne, (35.3 cu. ft.)

The percentage gain in weight by an oil on being hydrogenated =

$$\frac{\text{iodine value drop}}{127}$$

The heat liberated in hydrogenating an oil is sufficient to raise its temperature approximately 1.6°C for each unit drop in I.V. if the heat is not dispersed in some other way.

II. HYDROGENATION TECHNOLOGY

15. CLEANING THE CRUDE OIL

Crude vegetable oils may vary in their degree of unsaturation according to genetic strain and because of climatic regional differences. This is little problem to the hardener. With the crude oil may come dirt, moisture, phospholipids and protein material as gums or mucilage, free fatty acid and traces of metallic impurities. The edible oil refiner is concerned to remove these to obtain a bland oil (after subsequent deodorisation) in the most economic manner.

This review consideres chiefly those aspects of the treatment before hardening (pre-refining) which bear directly on hardening. In a modest plant of a few hundred tons oil per week treatment capacity, the same individual is probably responsible for refining and hardening; for many oils the pretreatment standards are kept virtaally the same as a matter of convenience whether the oil is due for deodorisation immediately or after hydrogenation.

Dirt must be removed for obvious reasons; moisture must be brought down to the usual level of 0.05% max. since it causes splitting of fat with increase in f.f.a. in the hydrogenation autoclave, injures active catalyst and builds up in the space above the oil in a non-circulating type system. Phosphorus and sulphur bearing impurities chemically attack active nickel whilst the same impurities may physically block the surface of the catalyst. In this connection some quantitative concept is very useful. Imagine 0.1% nickel/oil is present as catalyst and 1 p.p.m. sulphur in the oil. If all the sulphur in the oil passes onto the nickel this amounts to an increase of only 0.1% S/Ni. Any reasonably durable commercial nickel catalyst withstands an increase of about 3.0% S/Ni before its activity has dropped to about 10% of the original value.

Apart from rapeseed oil and oil from other brassica crops whose sulphur content may still remain in the 30 p.p.m. region after pretreatment, most vegetable oils do not contain more than a few p.p.m.

of sulphur. Lecithin and related phospholipids are removed by one or other method of degumming - dilute phosphoric acid treatment, hydration etc., - so that the phosphorus is brought down to the same low level as for sulphur mentioned above. Evidently the nickel catalyst suffers physical damage, some blocking of pores, attack from breakdown products from triglycerides, during its working life with vegetable oils, and the same build-up of sulphur found when hardening animal and marine oils is not experienced. To maintain isomerizing effect experienced hardeners have for long been accustomed to add very small amounts of sulphur to the catalyst during its working life in helping produce hardened vegetable oils of the steep dilatation curve (shorter melting range) class. Free fatty acid may indeed attack active nickel, but since it is general practice to reduce f.f.a. to less than 0.1% in the first refining operation this is not a problem; oil with much higher f.f.a. hydrogenates readily - possibly at the cost of some extra nickel, but this f.f.a. must then be removed after hardening. Finally it may be said that soap is one of the enemies of good hardening and good filtering, so the usual precaution to limit it to 0.05% max. before the oil is dried and earth bleached is reasonable: often much lower soap contents are attained.

In short, moisture and gums are the first things to control.

16. NEUTRALISATION

The conventional batch process of alkali refining, allied if necessary with gum removal via hydration, gives an oil easy to hydrogenate. New refining techniques look to superior yields of neutralised oil with some substantial improvement in quality in the sense of less oxidative damage to the oil being refined. The continuous centrifugal refining system may include at its fullest a preliminary phosphoric acid injection of about 0.08%, strong (ca 3N) alkali addition, weak alkali wash followed by hot water wash, continuous drying then bleaching earth addition before filtering. The refining factor (total fatty matter lost v. free fatty acid removed) is found in practice to be so improved as to more than pay for the additional capital cost and power consumption. Crude oils with low gum content (0.2% and less) may need no preliminary degumming additive and it may be possible to omit one washing stage. Continuous counter current alkali refining depending upon gravity separation of soapstock has been developed and in some instances is operated above the boiling point of water.

A wetting agent to promote even better separation of soapstock from neutral oil in a centrifugal system has been used by some refiners. The relative prices of neutral oil and acid oil, and the original level of f.f.a. must all be considered when deciding if the additional cost is justified. Where the crude oil arises from a solvent extraction plant a 65% oil:35% hexane miscella has been alkali refined in a hermetic centrifugal system to yield oils such as cotton and soya whose quality fits them for deodorisation and hence obviously for hydrogenation. Where there is particular need to lose the minimum of neutral oil in refining a valuable crude, separation of the fatty acid can be attained continuously on the full plant scale by counter current extraction of the fatty acid with methanol, ethanol or isopropanol. Finally if the crude oil is degummed and bleached first, systems have been developed whereby fatty acid and odour may be simultaneously stripped by steam at especially high vacuum (0.5 mm), or higher than average temperature (260°C). It will be abundantly evident that some recent systems are arranged so as to produce edible liquid oils in particular circumstances, hence the hardener must make his selection bearing in mind that following hydrogenation a post refining stage is to follow in any case.

17. HYDROGENATION - BATCH SYSTEMS

Since hardening is achieved on the surface of the catalyst by hydrogen which has made its way there from physical solution in the oil the first consideration is to disperse hydrogen effectively into the oil. A good gas/oil interface has to be maintained; higher pressure promotes higher rate of solution of the hydrogen and hence encourages a higher reaction rate up to the maximum possible with the particular amount of catalyst surface which has been made available. A minimum amount of nickel is likely to be 0.03% Ni/oil; most hydrogenations of edible oils do not exceed 0.10% fresh nickel. If the nickel is being continually re-used, several times this concentration may be present. Too many autoclave designs have been employed in the past sixty years to be listed here. The general philosophy is to disperse hydrogen from a gas sparger near the bottom of the autoclave then,

(a) expend power to so disperse the gas by flat blade turbines that the very small amount escaping into the headspace of the autoclave is easily sucked back by the vortex in the oil surface,

or (b) disperse the gas by stirrers but expend most power in creating surface agitation so that headspace gas is being vigorously mixed with oil,

or (c) allow gas to circulate from headspace via fat catcher, cooler and compressor to bottom sparger.

Systems (a) and (b) are closed and simple; they require a pure rather dry hydrogen to be practical; (c) is a circulating system better able to cope with less pure hydrogen but more elaborate. Since electrolytic and reformed hydrocarbon hydrogen are more than 99.5% pure and dry and are widely available the closed systems of hydrogenation are steadily replacing all others Power expended for normal batch hydrogenators in agitating or agitating and circulating should not exceed 1 KW/ton. A good average rate of hydrogenation would be 1 unit I.V. drop per minut If we allow for double this rate at the outset the exothermic heat generated would then be sufficient to lift the oil temperatu some 3°C per min. Obviously the heating/cooling coils must be adequate to control such an amount of heat and allow a constant temperature to be maintained at any level. A common working temp erature is 180° - 200°C, although the hydrogen might be introduc at the start at about 140°C. If the formation of trans isomers to be discouraged so as to obtain a relatively flat type dilatation curve (shortenings) the temperature is not allowed to exceed 150°C and may well be lower. Polyunsaturates if present are prevented from forming cyclic compounds by restraining the earlier part of the hardening to 150°C max. The course of the hardening can be followed by observing the drop in refractive index from a series of samples, each observation requiring about five minutes. Continuously operating refractometers are available. The end point is normally checked by I.V. or quick measurement of slip point. Filtration temperature should not exceed 100°C; closed filtration units have the advantage of excluding contact with air. It is best to blow filter lines and filter units clear from oil by using an inert gas such as nitrogen which is certainly safer and may be cheaper than hydrogen.

It is possible to displace the hardened oil from the autoclave into a closed, holding vessel. This may be done after the oil has been cooled to filtration temperature (100°C) or before. In the latter case the hot oil gives up its heat in a heat exchanger or to cooling coils in the holding vessel itself. Such a system saves 1 - 2 hours in a hardening cycle of 7 hours. One such holding vessel will service three hardening autoclaves.

18. HYDROGENATION - CONTINUOUS SYSTEMS

It is significant that whereas continuous neutralising and continuous deodorising units have been widely popular for many years continuous edible oil hardening units have not gained the same degree of acceptance although many designs have been advanced since the early years of the industry. Part of the explanation is that the batch autoclave (5 - 20 tons) is rightly seen as a flexible tool with which to produce a wide variety of hardened oils within a weekly programme. There is also the very important consideration of selectivity. In a continuous hydrogenation system there is a distribution of residence time with the result that a minor portion of the oil flow passes through a little more quickly and is not so completely hydrogenated as the remainder, whilst a corresponding amount remains rather longer than the average and becomes harder. In the case of vegetable oils the minor portion of the less hardened material may not create a significant flavour stability problem - this partly depends on how unsaturated the soft oil is and how far the mean hydrogenation is intended to progress. The slightly overhardened material will tend to elevate the m.p. and flatten the dilatation (SFI) curve, but not necessarily to an unacceptable extent. Fixed bed catalysts whose pellets offer the possibility of deep pores and hence poor selectivity for another reason (see para 23) are not in favour. Also the fixed bed catalyst changes steadily in use and must eventually be renewed. Controlling this situation raises additional problems.

It is evident that for end products which are nearer to the state of complete hydrogenation selectivity problems become relatively less acute. For the great majority of hydrogenated edible oils, i.e. those in the 30° - 40° m.p. bracket selectivity is important and most of the dozen or more continuous hydrogenation systems that have come into commercial use depend upon a catalyst in oil suspension moving through a series of separate agitated reaction vessels in which the gas/liquid mixing is obtained by stirrers, pumps (which may also transfer oil flow from stage to stage), or the motion of the gas itself. Not less than 3 and often up to 6 reactors are provided; these are arranged as a horizontal row or stood vertically upon one another forming a column. Frequently hydrogen is fed to each stage separately. Good agitation and more stages have improved the selectivity situation and it may also be that the preferential absorption of polyunsaturates on the catalyst works in the same direction by narrowing the distribution of residence time as far as they are concerned. Hardening can progress at one temperature (e.g. 150°C) and then be raised to another (e.g. 180° - 200°C) at a subsequent stage.

The advantages to be gained from a continuous hydrogenation system are,

(a) better opportunity for heat exchange from the exothermic reaction,

(b) shorter reaction time at high (180 - 200°C) temperature,

(c) greater utilisation of the total reactor volume which is therefore about half that of the batch equivalent,

(d) with careful control a steady flow of consistent product,

(e) some saving in labour.

In a varied production programme the continuous unit may have to be accompanied by one or more batch vessels to maintain satisfactory flexibility of the entire installation and avoid too frequent interruption of continuous feeding for very short runs on different feedstock. The continuous unit suits the factory whose programme includes a fairly large regular output of a single quality of hardened oil. For the rest, a batch system will generally be most acceptable. Catalyst is conveniently removed from hardened oil (batch or continuous production) by automatically assisted filter presses or other automatic units. The filtered catalyst is dropped into soft oil for re-use within a short time or is discarded if exhausted. Some factories discard a set proportion at intervals and make up with fresh catalyst.

19. POST-REFINING

After filtering the crude hardened oil it has been customary to treat it with a dilute alkali wash followed by a hot water wash so as to reduce the f.f.a. to less than 0.1 . This is because there is a slight tendency for f.f.a. to rise during hardening. This is the routine in batch equipment; in continuous centrifugal equipment one hot dilute alkali wash may well suffice. After, there follow the usual drying, earth addition and filtering. Finally the oil is deodorised.

Especially in the case of hardened vegetable oils the duration and temperature of hardening do not lead to much increase in f.f.a. - it may still be near the 0.1 level. In this kind of situation many plants omit the alkali neutralisation and merely make a light addition of an activated earth to reduce the nickel from 2 p.p.m. to about 0.1 p.p.m. before filtering a second time. Alternatively the second or 'polishing' filtration may be through a precoated filter. The oil is then deodorised in such conditions that the f.f.a. is stripped to ca. 0.03% simultaneously. A vacuum up to 6 mm. and temperatures above 190°C procure this effect in batch deodorisers; the task is even easier in many continuous deodorisers.

In batch deodorisation the total steam consumed in heating the oil, raising and maintaining vacuum and stripping the oil amounts to 40 - 50% of the weight of the oil. Of this steam only about one twentieth is needed for stripping and the time taken is from 3 to 5 hours. It is normal for continuous deodorisers to exchange the heat from the outgoing hot oil to the incoming cool oil. The oil layer is much more shallow, contact with steam more effective, temperatures may be higher and vacuum very good, hence residence time is reduced to less than 2 hours and in some designs less than 30 minutes. Continuous deodorisers are considerably smaller than batch units of equivalent rate of output. The savings of steam in heating and vacuum raising may therefore be as much as 50% of the batch requirement. Over twenty commercial types of continuous deodoriser are available. Several of the most successful are semi-continuous in their operation since oil is programmed to move from one shallow tray to another in sequence at fixed intervals, all trays, whether used for initial heating/deaerating, steaming or final cooling, being held in a common shell under vacuum. This gives such a plant operational flexibility; it may be arranged to operate in a truly continuous manner of uninterrupted flow from tray to tray.

Hardened vegetable oils have been very completely cleaned from gummy impurities by the time they reach the final stage of deodorisation and their inherent thermal stability is good. They are therefore well suited to the possibly higher temperatures of continuous deodorisers.

20. PROTECTION AGAINST OXIDATION

Although exclusion of contact with air is the best practice, one of the precautions which is becoming popular is to sparge a high purity nitrogen as very fine bubbles into the flow of oil as it passes along a pipeline into a holding tank. The volume of nitrogen introduced is about half that of the oil which it effectively strips from dissolved oxygen. The headspace in the holding tank is maintained as a nitrogen blanket. This precaution is more relevant for unhardened refined oils but could sensibly be applied to lightly hardened oils.

Metal sequestrants such as citric acid can be added at any convenient time after filtering and usually at the beginning of deodorisation. The development of many off-flavours arising from oxidation can be suppressed for a time by antioxidants such as BHT and BHA, usually limited to about 200 p.p.m. in total, but some of the hardening off flavours such as LHF are detectable at concentrations of 10^{-10} which is beyond the reach of effective action by anti-oxidants.

21. OTHER HYDROGENATION ROUTES

In the presence of conventional nickel catalyst hydrogen is added onto unsaturated oils by hydrogen donors such as iso propyl alcohol which itself becomes di methyl ketone in the process. This is described as conjugated hydrogenation. The ketone is capable of being reduced back to iso propyl alcohol. This oil hydrogenation proceeds slowly at room temperature, more quickly near the bp. of the alcohol (82°C) and very rapidly in the alcohol vapour phase. Other secondary alcohols gives this effect. Lower primary alcohols have also been found to react similarly in experiments at up to 20 atms. with methyl linoleate, but soon after the saturated fatty acid ester formed interesterification began. Octyl alcohol would act as a donor but did not interesterify. As yet there appears to be no industrial exploitation of these interesting reactions which are capable of exercising considerable selectivity.

22. SECURITY IN HYDROGENATION PLANTS

Risks in a hydrogenation plant should be assessed on the same basis as in other kinds of plant, that is, what is the probability of an event occurring and how serious would be its effect. Mixtures of hydrogen and air are flammable within certain proportio usually with explosive violence

For dry gases at 15°C and 760 mm. the lowest concentration of hydrogen which will sustain an explosion is 4.1% by volume (95.9% air). The upper explosive limit of hydrogen is 74.2% (25.8% air). Temperatures above 450°C or contact with an active catalytic surface promote combustion.

Increasing pressure and/or temperature tends to widen the explosive limits slightly. For hydrogen/oxygen dry mixtures the limits are similar. If the gas is saturated with moisture the lower hydrogen limit is very little affected but as the proportion of water vapour increases with rise in temperature it is the oxygen proportion which falls. In the continuous monitoring of a hydrogen supply the alarm condition is obviously always set well below the critical level. Thus 2.5% air might be chosen, since this nevertheless indicates an abnormal condition which might deteriorate to a dangerous one.

The basic precautions are, (a) prevent hydrogen from leaking out, (b) prevent air leaking in, (c) avoid ignition. Ventilation must be good; siting units in the open air if otherwise feasible is good. When inside, items of plant handling hydrogen should be placed as high as practical. This avoids having to apply the mos stringent protection to electrical equipment on the ground. Autoclaves should not be emptied by using hydrogen pressure, nor shou lines be cleared by hydrogen blowing. Leaks at glands and joint can be detected by application of soap solution. Observation of gas holders over a shut down, such as a week-end, will indicate if any movement (leaks) takes place over and above that due to temperature changes. On feed lines to autoclaves such as oil an catalyst slurry lines it is wise to fit two valves in series wit a small vent between them which is opened when the two valves ar closed. Major vents, such as those associated with safety press relief valves, should be directed to the open air and fitted with flame arrestors which must be earthed and of approved design. They must never be pointed towards sensitive equipment. Gas holder level alarms are considered at para 40; the aim is to maintain a positive internal pressure of hydrogen in all hydrogen handling equipment at all times when the equipment is not open for inspection or repair. Compressed air supplies must never be connected to lines which lead back to an autoclave. If vacuum is used in the system this should be done by steam ejectors for preference. Lines and plant items should be purged with an inert gas such as nitrogen.

When an autoclave has to be opened the interior must first be freed from catalyst by stirring a normal oil charge in the autoclave. At this point the gas space may be purged free from hydrogen by nitrogen, then as the oil is withdrawn to another vessel nitrogen takes its place. Alternatively, if no nitrogen has been used it is also a common safe practice to withdraw the oil and then completely fill the autoclave to overflowing with water, hydrogen being driven out to atmosphere. When the water is drained away air is allowed to enter. In either event, the interior of the autoclave may then be easily cleaned, after the top manhole has been opened, by filling up with hot water in which some sodium carbonate has been dissolved. [illegible] nitrogen [illegible] be replaced by air before entering the autoclave.

Prior to being entered the autoclave must be blanked off from all inlets and outlets (closing valves is NOT sufficient); these include hydrogen lines (HP and LP), waste gas, soft oil, vacuum (if any), outlet and catalyst addition line (if any). Air is blown in if necessary to cool the interior. Fuses must be removed from the immediate circuits controlling agitation gear so that this cannot be accidentally switched on. When repair has been completed air is either expelled by water filling and hydrogen drawn in as water is drained out, or oil is filled into the autoclave and the gas space purged free from air by using nitrogen. Nitrogen is then replaced by hydrogen.

No matches or lighters should be allowed in the hydrogenation plant area. Welding during production periods in the hydrogen risk area should not be allowed. It is advisable to use tools that are unlikely to produce sparks in an area where there is a risk of igniting gas. The area, in any case, should firstly have been completely cleared of inflammable gas. If gas trailers are employed these must be earthed before discharge commences. The vehicle should not be capable of being started up whilst still connected to the permanent installation.

Classification of hazardous zones has exercised considerable attention internationally in the last few years. Recommendations now exist for such areas and these are listed below.

Zone 0 - an area or enclosed space in which a hazardous gas or vapour or volatile fluid is present in sufficient quantity at all times to constitute a flammable concentration.

Zone 1 - an area or enclosed space in which a hazardous gas, vapour or volatile liquid of flammable concentration may be released from time to time during <u>normal</u> operation.

Zone 2 - an area or enclosed space in which a hazardous gas, vapour or volatile liquid, is so well under control that a flammable concentration can only be present in <u>abnormal</u> operation.

The basic considerations before classifying a risk, although obvious are given below:-

(a) Is there a flammable substance involved in the proposed process?

(b) What quantity is involved and what are its chemical and physical properties?

(c) How is the substance being stored and used ("closed" or "open" process)?

(d) Is the process plant contained within a building or is it outside?

(e) What is the proximity to neighbouring plant, third party sites, and sources of ignition?

III. CATALYST

23. SUITABILITY OF CATALYSTS

A catalyst must offer a high specific nickel or other active surface, easily accessible to triglyceride molecules (ca. $15A^{o}$ width), to promote good hydrogenation reaction rates. Active nickel catalysts are known to contain nickel crystallites in the $50A^{o}$ - $100A^{o}$ range which infers a specific surface of some 90 m^{2}/grm. Ni. On their own, such small particles would present a hopeless filtration task, but distributed in some porous support, such as that derived from the siliceous deposit kieselguhr, the resultant impregnated particles can be produced in the 1 - 10 micron (10^{4} - $10^{5}A^{o}$) range. These supported catalysts filter rapidly and providing the usual precaution is taken of filtering for the first ten to fifteen minutes at a slower rate to allow some filter cake to build up, the 'black run' is small and can easily be clarified by being refiltered on the same press. This catalyst is mechanically robust and can be used forty times or more without necessarily giving filtration problems, although its activity is such, after the first five or six uses, that it is best fitted for light hydrogenations involving merely up to 30 I.V. drop. Catalysts with high specific nickel surface can absorb appreciable amounts of poison and still remain sufficiently active to promote hydrogenation at an acceptable rate over several uses. Also in the case of free fatty acid hydrogenation, where the molecules involved are much smaller than those of triglycerides, if a proportion of this active surface is located well inside pores which admit fatty acids but not most of the sulphurous or other impurities the catalyst will be particularly durable if not selective.

Selectivity in fatty oil hardening has already been shown (para 8) to depend upon the ability of the more unsaturated triglyceride molecules to desorb and completely escape from the vicinity of the catalyst surface after only one double bond has been hydrogenated or isomerized. If the catalyst pores are relatively narrow ($20A^{o}$ of less) and perhaps long (possibly some hundreds of A^{o}), there is every chance that more than one double bond is hydrogenated during the residence time of the molecule in the pore. This means the progressive orderly decrease of unsaturation in the oil as a whole is lost. In these circumstances individual saturated fatty acid groups and even saturated triglycerides begin to appear much earlier in the reaction. Pores whose width is $25A^{o}$ or greater allow a much freer movement of triglyceride molecules in and out; hence they establish greater selectivity. Selectivity is influenced by pore width on the one hand and by the size of the molecules being hydrogenated on the other.

Where particles of nickel are produced by the thermal decomposition of organic salts, such as the formate, many are extremely small and may form aggregates. The same considerations regarding selectivity apply to these unsupported particles. However, probably only a minor portion fall in the 1 - 4 micron size range and the majority fall below this range. This can easily give rise to problems when the hardened oils made with such catalysts come to be filtered. The usual answer is to employ some filter aid which it is a common practice to add to the catalyst at the time of preparation. When the catalyst is re-used, especially if it has acquired some supporting filter aid, at one time or another, the question of filtration becomes much less difficult and behaviour approximates to that of a supported catalyst.

24. RANEY NICKEL

When the aluminium is leached from a 50/50 nickel/aluminium powdered alloy by a solution of caustic soda the nickel remaining is an active catalyst. After careful water washing followed by drying in the absence of air the catalyst is used not only to hydrogenate oils but for other industrial hydrogenations. This catalyst is markedly pyrophoric when exposed to air. Although often used in the laboratory it is not nearly so commonly used in industrial oil hydrogenation as the kieselguhr and formate catalysts mentioned above.

25. NOBLE METAL CATALYSTS

Palladium, rhodium and platinum are much more active in promoting hydrogenation of oils than other related noble metals. Since palladium is not only the most active but the cheapest of these metals it is the obvious first contender for industrial use. Palladium has been variously estimated as being 20 to 100 times more active than nickel; no doubt the result depends upon the condition of the catalyst and the circumstances of the test. Certainly it is much more resistant to attack by free fatty acids than nickel, but its activity is steadily reduced in the presence of poisons, such as sulphur compounds, which also damage nickel catalyst. It produces a high proportion of trans isomers, appears to encourage migration of double bonds and is selective. Since it is very costly as well as very active the obvious answer has been to disperse it thinly on some inert support such as carbon, so as to adapt it for industry. So far, in spite of its interesting technical performance it has not achieved large scale use.

26. COPPER CATALYST

The catalytic activity of copper has been known since the researches of Sabatier and Senderens and the possibility of enhancing the performance of nickel catalyst by incorporating copper has been pursued intermittently by various oil hardeners since that time. In the last fifteen years investigation of the superior selectivity of copper catalysts has been intensified, sometimes in association with other metals as in copper chromite, but not with nickel. The best copper catalysts will promote a hydrogenation rate of linolenate (triene) which is up to 15 times greater than the rate at which linoleate (diene) is hydrogenated, whereas the corresponding selectivity of nickel is little better than 2.

Conjugation of double bonds prior to their reduction has been advanced as the mechanism by which the very selective hydrogenation with copper proceeds. Conjugated or conjugatable dienes are reduced further to monoenes but there the hydrogenation ceases. This behaviour has made it possible to eliminate linolenate from soyabean oil whilst conserving much more of the valuable linoleate present than can be achieved by any nickel catalyst. Also marine oils have been hydrogenated to stable liquid oils. Copper catalysts must be entirely segregated from plant handling nickel catalyst if they are to preserve their selective efficiency; also it is important to remove copper promptly from the filtered hardened oil by a phosphoric acid wash or absorption on an activated earth. As yet copper catalyst has not been made with the same re-use potential as nickel catalyst. Linolenate containing oils hydrogenated with copper catalyst must face competition from the natural vegetable oils whose unsaturation is present only as linoleate and oleate.

27. RECOVERY OF NICKEL FROM EXHAUSTED OR "SPENT" CATALYST

Spent catalyst usually contains about 55% hardened fat which is best removed by solvent extraction, in which case the value of the recovered fat largely defrays the cost of the extraction. Less desirable procedures are to combust the fat, saponify it or separate it from the liquor following acid digestion of the fatty catalyst cake. The nickel bearing portion is then boiled with a somewhat diluted commercial sulphuric acid for a period which may vary from 3 to 12 hours until all but a very resistant 3% or thereabouts of the nickel present has passed into solution. Oxidising agents speed the attach of the acid. The liquor is then made only weakly acid by the gradual addition of sodium carbonate and filtered. From the slightly acid solution of the nickel sulphate any iron impurities, if present, may be precipated as hydrated ferric oxide by the cautious addition of more sodium carbonate - the nickel sulphate still remaining in the solution which is filtered.

28. CATALYST PRODUCTION

The most common starting point for the production of nickel catalyst is a solution of nickel sulphate although nickel nitrate has been used when the continued presence of the sulphate ion at later stages was held to be objectionable.

(a) Dry reduction

A complex basic nickel silicate accompanied possibly by hydrated oxide and carbonate is precipitated at or very near boiling condition from the nickel sulphate by the addition of an alkali such as sodium carbonate, bicarbonate or hydroxide in the presence of a siliceous material, kieselguhr being usual for this purpose. The kieselguhr also acts as a support for the precipitate. The operation may be organized on a batch or continuous basis. Good agitation throughout the precipitation vessel is important.

At the next stage the precipitate is filtered and liberally washed to minimise sulphate content. The cake when discharged will contain 55 - 63% moisture. Various drying procedures are used to reduce this moisture to less than 5%. Local overheating or baking to hard coarse nodules is to be avoided and this presents no special difficulty. The powder is next fed continuously into a roaster of the tubular or pyrites burner type where it is agitated in a flow of hydrogen at 430° - 500°C. The continuous hot discharge of pyrophoric nickel catalyst, still under an atmosphere of hydrogen, is dropped directly into a stirred vessel containing whatever oil has been chosen as the medium for the final catalyst. A well hardened oil is most suitable for this purpose since not only is it stable but the resultant catalyst may eventually be fed to a chilling drum and flaked. The flaked catalyst is immediately packed into drums or other impervious containers. Pyrophoric catalyst may be collected in an inert gas and then rendered passive (non-pyrophoric) by controlled exposure to air whilst being agitated. It must be packed promptly and held in impervious containers such as small drums.

(b) Wet reduction

Nickel formate has a very low solubility in cold water and hence may be conveniently prepared by adding sodium formate to a strong solution of nickel sulphate. The nickel formate thrown out of solution is filtered, washed in the minimum of cold water to remove sulphates of the mother liquor, air blown, dried and then packed as the crystalline, $Ni(HCOO)_2 2H_2O$.

Precautions must be taken to conserve any nickel salts remaining in filtrate liquors. Alternatively nickel formate is made by the direct action of formic acid on nickel carbonate or hydroxide. Since the thermal decomposition of nickel formate may be carried out in a comparatively simple type of plant it has been popular with hardeners who wish to prepare their own catalyst on site. The production unit consists essentially of a closed vessel equipped with stirrer, heaters, temperature recorder and vent pipe. Nickel formate crystals are added to about twice their own weight of oil in the vessel with agitation. A partly hardened oil is very suitable. The vessel is closed and heating commences steadily until a temperature of 180°C is reached when water of crystallization is driven off with a consequent spontaneous flattening of the rise in temperature. This condition is held for almost an hour when the temperature again shows signs of rising. More heat is applied until the temperature is nearing 240°C when some of the applied heat is turned off so that a steady 250°C is attained and held. Temperatures above 255°C damage the quality of the catalyst.

Decomposition of the nickel formate is now well underway and carbon dioxide, hydrogen and steam are evolved. During this period a steady current of hydrogen is passed through the vessel to expedite the escape of the decomposition vapours up the vent pipe. Some plants prefer to apply vacuum for this purpose. Decomposition is complete within 1 - 2 hours. The vessel is cooled to 90°C, kieselguhr may be added, then it is emptied. The suspension of active nickel may be filtered to produce a cake of active catalyst. If desired this cake may be slurried in fresh oil.

29. STORAGE AND HANDLING OF CATALYST

For many years nickel catalyst was made available to hardeners as a fatty cake or concentrated slurry packed in drums. More and more a preference has been established for catalyst to be available in the form of thin flakes which are easily incorporated into liquid oil prior to hardening. Apart from ease of handling in this form it is possible to exercise a more exact control on the introduction of fresh catalyst into the hardening plant. The catalyst may be of the dry reduced variety on a siliceous support or of the formate type in which a filter aid has already been incorporated. When stored in sealed containers such catalysts retain their activity over many months, or even a few years. Fresh catalyst should not be left exposed to the air once the container has been opened since a gradual process of oxidation extending over days will reduce the activity.

Similarly during the period a catalyst is being repeatedly reused it is incorporated into a slurry with unhardened oil each time a filter unit is cleared. Dispensing of such a slurry should be completed within two or three days and this is usually no problem since the filtered catalyst is normally required again within hours. Multi wall impervious bags have proved perfectly successful for the transport of fresh catalyst flakes. If drums are used they afford a convenient means of returning the spent catalyst to the manufacturer for recovery of the nickel. Spent catalyst should be repacked very soon after it is discarded since when left in the open, exposed to air currents and hot sun, it constitutes a real fire hazard comparable with bleaching earth residues from a refinery.

30. INFLUENCE OF CATALYST QUALITY ON HYDROGENATION AND THE CONSUMPTION OF NICKEL

Catalyst quality is described in terms of activity, selectivity, durability and filtrability. These characteristics frequently relate to the duty for which the catalyst is employed: paras 8 and 22 have already considered how conditions at the catalyst surface and its general structure affect the course of the hydrogenation reaction.

Activity is related directly to the amount of active accessible nickel surface per unit weight of catalyst. This is by no means the same thing as the nickel content or the total specific surface. Laboratory activity measurements are routine empiric procedures in which a known concentration (dose) of nickel as the catalyst under examination is introduced into a standard weight of oil in a standard item of apparatus, stirred at a constant rate and through which a set number of litres of hydrogen per hour is bubbled. The temperature is fixed, usually at 180°C and the duration is commonly 30 mins. Pressure is normally atmospheric. The drop in refractive index or iodine value during the 30 mins. is observed and is a measure of the activity of the catalyst in these particular circumstances. Because its relative freedom from catalyst poisons avoids introducing complicating factors, sesame oil is a favourite oil for these tests. If the concentration of test nickel to achieve a certain degree of hydrogenation in these circumstances is compared with the concentration of some standard nickel which achieves the same effect, the activity of the test sample may be expressed as a percentage of the standard. If the type of catalyst is kept constant two samples of oil may be compared as regards hardening performance by the same routine. The test could be adapted to comparisons of two qualities of hydrogen if one were suspected of containing appreciable catalyst poison.

Selectivity has already been explained (para 8) as the ability to hydrogenate polyunsaturated groups preferentially. Isomerization to the trans form makes itself apparent at the same time in the conditions which favour selective hardening. Analysis by Gas Liquid Chromatography shows how the production of saturated groups is restrained by a selective catalyst whilst monoenes increase. A selective catalyst can thus achieve a greater I.V. drop for the same m.p., or for the same I.V. drop, the m.p. is rather lower, whilst the dilatation curve will be appreciably steeper.

Durability, which includes the resistance to poisoning, can be assessed by determining the minimum dose of catalyst necessary to achieve a certain degree of hydrogenation in what is arbitrarily selected as the maximum acceptable time. This maximum time is also a matter of plant economy since very long hardening times reduce plant utilisation. Durability and activity have some connection with one another because of their dependence on ample accessible active surface. In special cases a surface which tends to exclude poisons to some degree will have good durability. The concept of durability must include durability for what purpose.

Finally hardeners expect to obtain an overall filtration rate of 150 - 100 Kg. oil/m^2/hr. without particular trouble because of initial black run.

Vegetable oils are generally low (0 - 4 p.p.m.) in catalyst poisons such as sulphur and phosphorus, initially or by the time they have been pretreated. This means that for light hydrogenation tasks, such as hydrogenation of lauric oils, an initial dose of 0.05% Ni/oil would be ample. Since many re-uses would be possible, the overall consumption would drop below 0.02% Ni/oil. At the other extreme where it was felt necessary to produce a fully hardened vegetable oil, which involved an I.V. drop of 90 - 130 units within about five hours gassing time, an initial dose of 0.1 - 0.15% Ni/oil as fresh catalyst would be ample. This catalyst might be used again for similar purposes at treble the concentration, and finally pass to easier tasks in the general hardening programme. The expenditure of nickel on the production of the fully hardened oil would then be assessed at about half the initial dose, say roughly 0.08% nickel or 0.8 Kg. Ni/tonne oil. Finally it should be pointed out that for many hardened vegetable oils whose m.p. is in the 32° - 36°C slip m.p. range, catalyst can be used repeatedly, so that the overall consumption drops below 0.05 Kg. Ni/tonne oil, i.e. 10 - 20 re-uses.

The usage of nickel depends upon how the hardening programme is made up; without this knowledge no set figure can be quoted. Oils such as rapeseed which have a higher sulphur content, say

50 p.p.m. S on crude oil and 10 - 20 p.p.m. on neutralised bleached oil, show higher catalyst usages for most melting points.

31. ECONOMICS OF CATALYST PRODUCTION AND THE PRICE SITUATION

Costs vary widely with the regional situation and time. Figures given here are typical of W. Europe in 1971 and are given as U.S. dollars per kilogram nickel.

(a) Nickel Recovery

The cost of 1 Kg. nickel in the form of nickel sulphate crystals ($NiSO_4.6H_2O \equiv 22\%$ Ni)...3.5 to 3.8 dollars.

The market value of 1 Kg. nickel in the form of spent fatty catalyst (Ni content ca. 20%) delivered to the buyer...1.6 to 2.4 dollars.

The difference between these two value levels indicates the cost margin within which a recovery process is obliged to operate. Many catalyst suppliers seek an agreement with their customers whereby catalyst is returned after use for recovery of nickel. If the nickel content is higher, (say 30%) the value allowed on the nickel is often increased by about 33% since extraction is more economic. Below 10% Ni content the spent catalyst may be easier to sell to other outlets. Where there has been no local demand for spent catalyst shipment several thousand miles to Europe has been worthwhile.

(b) Catalyst production

One starting point is nickel sulphate as costed above.

The cost of 1 Kg. nickel as nickel formate crystals ($Ni\ (H.COO)_2\ 2H_2O \equiv 31\%$ Ni) ... 5.2 dollars.

Cost of 1 Kg. nickel as fresh active catalyst in 25% Ni fatty flakes, ... 8 to 10 dollars.

Cost of 1 Kg. nickel as fresh active catalyst in 55% inorganic powder, ... about 11 dollars.

The performance of a catalyst in it's particular field of application is a distinct factor in deciding its price. The price range per 1000 Kg. active nickel is 8,000 to 14,000 dollars.

Assuming 0.2 kg. nickel, costing 2 dollars less 0.4 dollars (spent value), is consumed in hardening 1 tonne of oil, costing 360 dollars, it is evident that the catalyst charge amounts to about 0.4% of the oil cost. It is understandable that the great majority of hardeners should prefer to purchase catalyst rather than make their own.

IV. HYDROGEN PRODUCTION

32. HYDROGEN PURITY

Impurities in the hydrogen used for vegetable oil hydrogenation fall into two main categories. Firstly, there are inert impurities which merely dilute the hydrogen or otherwise obstruct the operation of the autoclave; secondly there are impurities which attack the catalyst and some may also encourage splitting of the oil.

Inert impurities mainly consist of non condensible gases such as nitrogen or methane. In a closed or 'deadend' system they accumulate in the headspace of the autoclave and obviously reduce the partial pressure of hydrogen contained there. Finally if the hardening continues far enough and the headspace is not purged, pressure in the autoclave equals that outside and hardening stops. Even in a gas circulation system inert impurities cannot be allowed to accumulate indefinitely since this lowers the proportion of hydrogen in the circulated gas, wastes energy and prolongs hardening. Water vapour derived from imperfectly dried oil, and possibly a little from the hydrogen itself, would also obstruct hardening if allowed to build up in the headspace, hence the value of drying oil below about 0.05% moisture/oil.

Fortunately the most widely used methods of hydrogen production now set a standard of 99.5 - 99.9% purity (dry basis) so the obstruction of the system scarcely arises and in any case can always be dealt with by purging at a moment when the concentrated impurities can be vented for the least loss of hydrogen.

Compression (to ca. 7 atms.) and cooling moist hydrogen effectively reduces the moisture to about 0.1%(v/v) at which level it will not significantly obstruct edible oil hardening or encourage serious splitting of fat. Sulphur is absent from electrolytic hydrogen and does not exceed 1 p.p.m. in hydrogen from reformed hydrocarbon. This is satisfactory since an active catalyst would survive several uses at many times this concentration of sulphur in the hydrogen.

Carbon monoxide should [illegible] as it can form nickel carbonyl. At 150°C the latter commences to decompose and CO begins to be eliminated from the metal surface. It is claimed that at 150°C 0.1% [illegible] is still harmful, but that at 180°C – 200°C even 0.5% (v/v) has little effect. Reformer hydrogen is processed so as not to exceed 10 p.p.m.; electrolytic hydrogen should contain no CO; hydrogen derived from electrolysis of brine might contain up to 0.3% CO depending on conditions under which sodium amalgam is decomposed by addition of water. For hydrogen drawn as a by-product from the electrolysis of brine in a mercury cathode cell system it is easy to keep the mercury content below about 10 microgrammes per cubic metre by passing the hydrogen (after its first compression and cooling which removes most of the mercury) through a carbon/iodised carbon scrubber. Even 100 microgrammes mercury per cub. m., if all transferred to the hardened oil, would not give rise to a mercury concentration above what is commonly found in many natural foodstuffs.

Oxygen and halogen are unlikely to be present in significant amounts in electrolytic or reformer hydrogen. Hydrogenations depending upon fresh catalyst, such as low temperature (below 150°C) hydrogenations, are also dependent on the purity of the hydrogen.

33. WATER ELECTROLYSIS

Pure water is a bad conductor of electricity but when substances such as potassium hydroxide (KOH) or sodium hydroxide (NaOH) are dissolved in the water a large current can be passed from one conducting plate (electrode) to another when these are immersed in the solution – (electrolyte). The dissolved substances help convey the current, but it is the water in effect which decomposes to its elements, hydrogen at the cathode plate (-ve) and oxygen at the anode (+ve). There is a strict relationship between the amount of chemical reaction and the amount of electricity passed through the solution in all reactions of this kind. Thus the passage of

2400 amperes for 1 hour produces 1 cub. m. of dry pure hydrogen measured at 0°C 760 mms. Hg. In more convenient terms, this is to say, that the hydrogen contained in 1 cub. m. of moisture saturated gas at 20°C 760 mms. Hg. would be produced by 2180 amp. hrs. To drive the chemical reaction forward an electrical pressure of nearly 1.5 volts (decomposition voltage) must be applied. At the same time three other voltages must be added to overcome anode resistance, electrolyte resistance and cathode resistance. The final value of the necessary cell voltage lies between 1.8 and 2.6v. according to the design of the electrolyser cell, the electrolyte used and the operating conditions, (temp., pressure, concentration).

NaOH is commonly specified to operate at 20% conc. and 60°C
KOH " " " " " " 28% " " 80°C

Up to 1.48v. the heat liberated by the flow of current is absorbed by the system. Above this voltage heat is given out, hence practical electrolyser designs must include provision for cooling coils. The range of energy consumed to produce 1 cub. m. moist H_2 (specific consumption) at 20°C and 760 mm. Hg., depending on the efficiency of the cell system will be,

from 2.18 x 1.8 = 3.92 kwh /cub. m. H_2
to 2.18 x 2.6 = 5.66 " " "

Cell manufacturers constantly seek designs which require the minimum over-voltage and hence consume the least current for the hydrogen produced.

4. THE RECTIFIER

Electrolysers operate on direct current hence alternating current bought from the national grid must first be rectified. Since the late 1950's monocrystalline semi-conductor rectifers based on germanium or silicon have been developed to such efficiency, coupled with low cost, that they are steadily superceding all other types of rectification. A wafer of monocrystalline silicon about 2 cms. in diameter is clamped between a thin section of molybdenum and a tungsten base mounted in a ceramic housing. When a voltage is applied in one direction very little current will flow and this blocking effect or inverse voltage may withstand over 2000v. When the voltage is reversed and reaches almost 2v, current begins to flow freely, increasing to 200 amps. (for the size of wafer mentioned) as the voltage increases. Single rectifiers carrying 300 amps. d.c. with forced air or water cooling exist.

Complete installation of conversion from High Voltage a.c. to Low Voltage d.c. is available at 31 - 48 U.S. doll. per kW.

35. THE ELECTROLYSER

Two basic types of electrolyser have been manufactured for many years. These are the Unipolar or tank type and the Bi-polar of "filter press" type. The sketches at Appx. 1 illustrate the basic principles of operation of each.

Unipolar type

Electrode plates are supported in a tank holding the electrolyte. Tanks vary in size according to the capacity of the whole installation, but 1.3 m. (length) x 1.3 m. (width) x 2 m. (height) approximately would be average. Each electrode is hung in a bell housing which collects the gas evolved; there is always one more anode than cathode in each tank.

An asbestos diaphragm (D) completely surrounds each cathode preventing any mixing of the gases. Each tank stands on insulators and is insulated from the next tank in the row. Electrodes in one tank are connected in parallel; tanks in a row are connected in series: this gives the most even distribution of load. In a typical unipolar battery the cells would require on average 2.1 volts and 4.58 kWhr./m^3 specific consumption; at slight extra cost this could be equipped to operate at 1.99v. and 4.34 kWhr./m^3.

Unipolar batteries are of simple construction and layout which greatly eases maintenance. Complete overhaul once in 60,000 hrs. running time can be carried out by local engineering staff, mechanical tolerances are reasonably large, operating current density is only about [illegible] amps/sq.m.

Several designs are open topped which means the alkali gradually carbonates and this leads to increased current consumption. Also many designs operate near atmospheric pressure so that a booster may be needed in the gas collecting systems. Two or three cells can be taken out of circuit for overhaul at any time with little loss to the overall capacity.

Bipolar type

A bipolar battery of cells is likened to a filter press because of its superficial appearance and arrangement, although of course it is several times larger.

As indicated in Appx. I the large sheet steel electrodes (P/N) divide one cell from another so that on one side the surface of a sheet acts as an anode, and on the reverse side it acts as the cathode of the adjacent cell. Not shown in the sketch are additional perforated plates raised slightly away from each surface but electrically connected with it, so that the electrode surface is considerably increased. These are the forward anodes and forward cathodes. An asbestos diaphragm (D) mounted in a frame separates anodic and cathodic compartments and is also insulated around the periphery therefore the great majority of the current can only flow from plate to plate via the electrolyte. Massive end plates are tightened up so that an evenly distributed pressure prevents leaks from the assembled battery.

The electrolyte surges up through the cells and in the gassing condition it overflows into the appropriate gas collecting manifold. The gas next separates and then the electrolyte, after being pumped through a filter, returns to the individual cells again via a distribution manifold. This flow detaches bubbles from the surface of the electrodes. This in turn leads to an improved specific consumption of power because the loss of electrode/electrolyte interface is reduced. A typical bipolar battery would have a cell voltage of 2.04v. and specific consumption of 4.1 kWh/m^3. The battery will usually operate at about 40 cms. water gauge pressure so that no booster is required. Cathodes are often given an activation treatment which reduces over-voltage slightly and saves 10% power. Although this effect may last for no more than 20,000 hrs. the expense can be justified, especially on a large unit. All bipolar units are closed so that contact of air with the electrolyte is prevented. There is a high output of gas from a small plant volume and they tend to be more efficient in terms of power consumed for gas produced.

To keep initial capital outlay economical the minimum number of cell blocks to meet gas output must be purchased but at least two are needed to avoid complete shut-down at times of major overhaul. Overhaul which should be every four years is much more expensive than for the unipolar battery and will occupy at least two specialists and six assistants for a minimum of two weeks, presuming no parts have to be returned to manufacturer.

Mechanical tolerances have to be close and high current densities of 2000 - 3000 amps/sq.m. are used

High pressure (ca. 30 atms.) bipolar batteries are produced.

Because the bubble size is much reduced there is a saving in voltage and a consequent all-round saving in volume. An overall cell voltage for such a unit is quoted at 1.8[illegible]v. per cell and specific consumption [illegible].02 kW/h/m^3.

36. ELECTROLYSER WATER SUPPLY

A high standard of purity is required for the water fed to the electrolyser since the presence of certain mineral salts considerably aggravates the problem of corrosion.

The dry residue from the water feed should not exceed 10 milligrams per litre. The specific conductivity of the water should not exceed 6.67×10^{-6} reciprocal ohms per cm., that is, the specific resistance is not less than 150,000 ohms per cm. Water should be free from chloride, sulphate and carbon dioxide. Ordinary condensate may not meet these standards. Simple steam heated stills are available which in one distillation give a water quality whose residue is about 4 milligrams per litre and whose conductivity is as low as 4×10^{-6} reciprocal ohms per cm., i.e. specific resistance is 250,000 ohms per cm. Such stills should not operate above 75% rated capacity in case of carryover of feed water. A small ion exchange cartridge could be fitted after such a still and a much higher purity would result, but this is not really likely to be needed.

Demineralisation equipment can be used in place of the still depending on the quality of the raw water to be treated. Other commercial stills are available which re-evaporate condensed steam and this double effect also gives high purity.

37. HYDROGEN PRODUCTION CAPACITY AND STORAGE

The hydrogen demand of the largest edible oil hydrogenation plants can very easily be met either by electrolysers or hydrocarbon reformer units, (see also para 41). As mentioned at para 14, an allowance of 1 cub. m. H_2 should be made for a one unit I.V. drop for one metric tonne. The weekly tonnage of hardened oil multiplied by the average I.V. drop divided by the hours it is proposed to operate the hydrogen generating equipment gives the hourly capacity required. Ideally the equipment should be operated above 90% capacity. Seasonal peak demands can obviously be smoothed to a degree by building stocks of hardened oil and maintaining 168 hours per week working during the peak.

Hydrogen is delivered from the generating equipment to a low pressure holder unless the generator itself is already producing gas at several atmospheres pressure. The low pressure holder may contain only half an hour's output; the gas from it is compressed, cooled and put into a high pressure store such as a large sphere (up to 10 atms. say), or large horizontally mounted cylinders (above 10 atms.) The H.P. store is then the buffer store for the autoclaves. If the autoclaves work at 3 atms. and the H.P. store up to 7 atms. it is the difference of 4 atms. times the H.P. store volume which is the effective buffer. If this effective buffer is made equal to about 4 hours' hydrogen output it can be used very conveniently to cover short generator shut-down periods for adjustments and minor repairs; also, this buffer capacity will take care of hour to hour demand variations if the weekly plan has been properly drawn up.

38. HYDROGEN MEASUREMENT

Quantities of gas are stated in terms of volume hence the pressure, temperature, degree of purity on a dry basis and the amount of moisture present must be defined also. This is essential whether the hydrogen output of an electrolyser is being checked against the energy input, or the actual hydrogen used in a hardening programme is being compared with the theoretical figure. Where hydrogen is being purchased the same considerations must apply at the time a contract is made. Hydrogen may often be presumed to be saturated with moisture at the moment of manufacture (e.g. electrolysis of water), but subsequent compression and cooling before use or purchase will alter this. A statement of maximum permitted dewpoint is adequate; it may be checked as a routine at convenient intervals.

Numerous instruments depending on pressure differential are well known as flow rate indicators and their records may be integrated by hand or automatically to give quantitative measurements. Their accuracy is poor, often ±5%, only 1%± with extreme care. A positive displacement meter is to be preferred. A widely used type operates on the principle of the cycloidal blower. In the case of the meter, the movement of the gas flow rotates two interlocking elements so that a fixed volume of gas is passed through the meter for each rotation. There is only a small pressure loss of 1 - 2 cms. water gauge across the meter; accuracy is better than 1% (often better than 0.5%); pressure and temperature corrections have to be applied. Meters for various wide ranges of flow rate are available as well as elevated pressures. The small slip factor of the meter should be checked about once a year.

The quality of hydrogen may be monitored continuously by a Katharometer. Since hydrogen has a thermal conductivity some seven times greater than any impurity likely to be present this fact is exploited in comparing the cooling effect of the sample gas on a heated platinum wire with that of a pure hydrogen reference. The instrument is based on a Wheatstone bridge arrangement; the sample gas must first be passed through a drying tube. Warning signals and precautionary actions can be initiated from such an instrument in the event of the hydrogen purity falling below some pre-set level.

39. OXYGEN

The by-product oxygen arising from water electrolysis is likely to command a very attractive price - at least equal to that of hydrogen - in areas where there is no well established supply. Some, or all, may be bottled for use in the same factory. Amounts as low as 10 cub. m./hr. may be worthwhile collecting. Since the gas is wet as it leaves the electrolyser it may be held in the conventional wet holder until it is compressed for use or sale. Oxygen is more highly para magnetic than almost any other gas. Instruments exist for monitoring quality which are based on this property.

40. SECURITY

Deterioration of oxygen purity is the commonest early warning of trouble arising in an electrolytic plant. Normally oxygen purity is held at better than 99.0%. It is inadvisable to operate the electrolyser at oxygen purities less than 95.6%. Hydrogen and oxygen purity tests must be done at least once per shift if the purity is not being continuously monitored.

Normal values for cell voltages are,

	Unipolar				Bipolar		
(a) Anode-cathode	1.99-2.3	volts			2.0-2.25	volts	
(b) Anode-gasbell	0.6-0.9	"	*	Anode-diaphragm	0.35-1.65	"	**
(c) Gasbell-cathode	1.39-1.4	"	*	Diaphragm-cathode	1.65-0.35	"	**

* For the uni-polar battery if the size of the voltage drops at (b) and (c) as shown alter to such an extent that (b) tends to become 1.[illegible] - 1.4v. and (c) 0.[illegible] - 0.[illegible]. This change-over is an indication of possible cell failure.

** For the bi-polar battery consistent values less than 0.35v. or above 1.65v. indicate a risk condition is arising.

These voltages should be part of the regular running check on the battery. In addition to gas purity and cell voltage checks other points to note are, cell temperature, electrolyte strength and purity, gas header pressures, functioning of feed water and cooling/heating systems and the appearance of the cells. Manufacturers supply details of critical data relevant to their own plants.

Precautions must always be taken against mixing of gases. On the low pressure gas holder an ultimate high level switch should limit electrolyser plates to below gassing voltage or switch off altogether if this level has been reached. An alarm should be given as it will be necessary, upon starting up again, to purge to atmosphere for a short time until a check shows that normal gas purity exists. Then the gas may be passed to the L.P. holder. This precaution is comparable to starting up the battery after a more prolonged pause of several hours.

A high level audible/visible alarm of an almost full holder warns operators to reduce gas output. A half-way switch controls normal compressor on-off duty. A low level switch switches off compressors and warns operators - who may be able to increase gas output or reduce demand. An ultimate low level switch isolates electricity supply to the compressor if the low level switch fails. A gas holder may carry a stopper mounted inside the crown in such a way that in the last stage of its descent the stopper closes the mouth of the gas off-take pipe which looks upwards from just below it. Low pressure cutouts may be fitted in compressor suction lines.

Major electrical equipment should be kept out of hazardous

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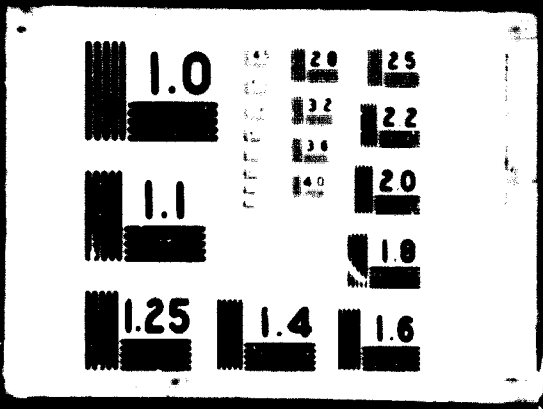


areas as far as possible; there must be good ventilation with no possibility of pockets of gas being trapped; pressure vents should be piped clear of the room to atmosphere. Steelwork should be bonded and lightning protection fitted. Galvanised iron should not be used in the vicinity (e.g. roof) of vapour from caustic alkali because of corrosion.

41. HYDROCARBON REFORMING

Most of the hydrogen used in edible oil hydrogenation is made from hydrocarbons such as propane (C_3H_8), butane (C_4H_{10}) or natural gas rich in methane (CH_4). This process has advanced rapidly in size and efficiency during the last ten years; at the same time the steam/iron process has become obsolete.

There are four main stages in the process:

(i) Desulphurisation

The hydrocarbon is passed through activated carbon at ca. 2 atms. and 20°C. This may be followed in more modern plant by passage over zinc oxide/cobalt molybdate/zinc oxide. Sulphur is reduced to 1 p.p.m. to protect the nickel catalyst at the next stage.

(ii) Reforming

$C_3H_8 + 3H_2O$ + heat = $3CO + 7H_2$

Propane + steam = carbon monoxide + hydrogen

In the low pressure furnaces, i.e. those operating at rather less than 1 atms. above normal atmospheric pressure, the hydrocarbon is mixed with about 7 times its own volume of steam and passed over a pelleted nickel catalyst in vertical tubes. The reaction can be carried out between 630° - 1100°C according to furnace design, catalyst etc. The hydrocarbon reacts with the excess of steam to give carbon monoxide, hydrogen and some other gases so that a typical analysis would be,

	% vol
CO_2	7.9
CO	19.7
H_2	72.1
CH_4	0.3
	100

(iii) Conversion

Low pressure steam is mixed with the reformer gas achieving a temperature of about 380°C and the mixture passed over nickel catalyst when most of the CO is converted to CO_2.

$$CO + H_2O = CO_2 + H_2 + \text{heat}$$

Since this is an exothermic reaction more L.P. steam is fed in half way through the converter to prevent a rise above 400°C. The composition of the gas then becomes,

	% vol
CO_2	21.86
CO	1.56
H_2	76.35
CH_4	0.23
	100

The gas is made to give up its heat in heat exchangers and coolers and is then scrubbed with methanolamine to remove CO_2.

The cleansed gas is then reacted a second time with steam, cooled and scrubbed so that after this second treatment its composition becomes,

	% vol
CO_2	Trace
CO	0.2
H_2	99.5
CH_4	0.3
	100

(iv) Methanation

$CO + 3H_2 = CH_4 + H_2O + Heat$

carbon monoxide + hydrogen = methane + steam

The gas leaving the second absorber is heated to 260°C and passed over a nickel catalyst when the reaction ensues as shown above.

The hydrogen leaving the methanators (260°C, 0.07 atms. above atmospheric pressure) is finally cooled and passed to a low pressure gas holder. It has the following composition,

CO_2	0.01% (vol.)
CO	10 p.p.m. max.
H_2	99.5% (vol.)
CH_4	0.45% (vol.)
Water vapour	Saturated

This standard of purity will enable any type of hydrogenation to be completed without difficulty. There have been significant further developments within the last six years. High pressure units which give a continuous output of hydrogen at 12 atms. 38°C have become common and are likely to become standard. One conversion stage is followed by a shift reaction over an iron-chrome catalyst. The gas is finally cleaned by absorbtion at high pressure of impurities such as CO, CO_2, N_2, CH_4 etc. in beds of carbon and molecular sieves of different types. This process is aimed at a 99.99% H_2 purity. Turn down capacity to a quarter or less of maximum can be arranged. Compressors to serve the hardening autoclaves are unlikely to be required, since the hydrogen is already at high pressure; heat recovery is much improved so that the plant becomes self sufficient as regards steam; smaller equipment is used; capital investment drops.

42. OTHER METHODS OF OBTAINING HYDROGEN

(i) Hydrogen may be purchased near established centres of chemical manufacture and moved by pipeline or trailer if distances are not too great. A large trailer carries the equivalent of 2000 standard cub.m. H_2 compressed to very high pressures. Definition of the quality standard and means whereby the quantity of gas purchased is to be measured must be agreed in the contract whatever the system may be.

(ii) Electrolysis of brine produces by-product hydrogen cheaply. Purity is discussed at para 32.

(iii) Petroleum refineries may have available large quantities of hydrogen in the waste products from certain types of operation. The waste gas can be cleaned up economically so as to be perfectly suitable for oil hydrogenation and would probably meet the following standard:- H_2, 99.3 - 99.7%; CO, Nil - few p.p.m; H_2S, Nil - few p.p.m; N_2, 0.1% max; O_2, 0.04% max; CH_4, 0.02 - 0.1%; ethane and assorted unsaturated hydrocarbons together not more than 0.001%.

(iv) Ammonia cracking in a tubular furnace at about 850°C over a special catalyst yields a 75/25 H_2/N_2 gas with maximum 0.05% undissociated ammonia. Passage through a palladium silver membrane produces a pure hydrogen. For full plant scale this process is likely to be much more costly than electrolysis or reforming.

43. SELECTION OF HYDROGEN PRODUCTION PROCESS

The usual choice is between hydrocarbon reforming or electrolysis of water. In turn, the economics of these methods depend upon cost and availability of hydrocarbon (including natural gas) compared with electricity.

For medium plants of about 200 cub.m. H_2/hr. output where there is no undue restriction on the supply of hydrocarbon a cost of 6 U.S. cents per cub.m. H_2 would be normal. As the plant size increases to some thousands of cub.m. per hour the cost drops towards half this figure.

Below 100 cub.m./hr. capital cost seems to affect the issue in favour of electrolysis so that at 50 cub.m./hr. the electrolytic cost of perhaps 12 cents per cub.m. (without sales of oxygen) looks more attractive. If circumstances are such that oxygen can be sold at least for the same price as hydrogen, then the electrolytic hydrogen costs are nearly halved. This means the electrolytic process remains competitive until much higher production levels are being considered. Hydrocarbon reforming units are on offer down to outputs of ca. 50 cub.m./hr.

Power consumption and capital investment for bipolar electrolytic units are usually lower than for unipolar units of the same hydrogen output. Maintenance costs are considerably higher, so that the initial advantage of the bipolar unit may be cancelled. The real criterion is the lowest cost for the production of a reliable supply of sufficiently pure hydrogen over a period of time. The versatility and ease of maintenance of the unipolar system have already been mentioned.

V. VEGETABLE GHEE PRODUCTION

44. GHEE

A little over one hundred years ago margarine was invented to supplement the supply of butter in France. Its manufacture grew steadily in quantity and variety until margarines established themselves as distinct products within their own right. About fifty years ago hydrogenated vegetable oils were introduced to Asia from Europe to supplement local supplies of ghee. A few years later the manufacture of hydrogenated vegetable oil or "vegetable ghee" commenced in the centres where the demand existed. Like margarine its production has increased enormously and it also is established as a product within its own right. India alone produces over 500,000 tons each year. To understand what is required of a vegetable ghee it is useful to consider briefly the origins and uses of ghee (milk ghee) itself. Butters made from the milk of cows, buffaloes, goats or sheep are difficult to store in the warm climates of the Far East, India and Pakistan, the Middle East and Africa. To ease this problem, both for the producer -(the farmer)- and the consumer -(the family)- the butter is heated steadily so as to make it possible to separate the fat from the aqueous phase by decanting the fat layer or simply evaporating the water. The flavour derives partly from souring of the original milk, partly from the protein - sugar interaction during the heating, which confers a caramelised effect, and sometimes partly from the smoky fire when the latter is used as the means of heating. Flavour may be described as cheesy, the odour as mildly fruity and the colour in some traditional varieties is a bright light yellow; in others, such as buffalo ghee it is almost white.

Moisture has been almost completely removed; some traces of milk protein may still remain. The separated fat is now allowed to cool and set to a solid. Depending upon how quickly the cooling takes place and the temperature of the surroundings the crystallization of the fat produces textures which vary from fine smooth grains to large grains, comparable with small rice grains, from which a little separation of some liquid oil may subsequently take place. With the considerable variation of starting material and mode of preparation it is only natural that the final product shows considerable regional differences.

45. VEGETABLE GHEE

Texture, melting behaviour and manner of use are closely related in the case of ghee. These same considerations must be taken into account when manufacturing a vegetable ghee which will meet customers' requirements in the same way or better. It is well known that neither ghee nor vegetable ghee is used as what in the west is called a spread. They are used primarily in cooking operations including deep and shallow frying, making of confectionery, baking, sometimes in curry preparation and much less commonly as a direct additive to food without any further cooking.

A typical ghee has a slip melting point of about 37°C; the melting behaviour is not too abrupt as may be judged from the following data:-

Temperature °C	15	20	25	30	35	39
Solid Fat Index	32	23.6	17.4	12.4	6.8	2.4
Dilatation	800	590	435	310	170	60

Obviously, if a vegetable ghee approximates to these characteristics in circumstances where ghee itself is satisfactory, then the vegetable ghee will be acceptable. If, on the other hand, ghee suffers some disadvantages in a particularly hot climate or does not give the best results in some baked product, that is good reason why a vegetable ghee should be modified slightly to meet the consumer's convenience. In the warm climates where vegetable ghee is in use summer temperatures can be such that 37°C is about the lowest melting point which will normally allow the product to remain solid in part, that is, comprising solid grains of higher melting components mixed with separated oil. This desire to maintain a solid product has been met sometimes by producing vegetable ghees with slightly higher slip points of up to 41°C. Since some milk ghees of 41°C s.p. occur such a vegetable ghee is still within the melting range of the natural product. At the other end of the scale there is no difficulty in making a vegetable ghee which melts around 30°C.

However widely the climate may vary in temperature the human body temperature remains close to 36.8°C. If a disagreeable persistent fatty sensation on the palate is to be avoided then the proportion of solid remaining in the vegetable ghee above this temperature must be strictly limited. This means that the SFI or dilatation is already low and falling gradually as it nears the 37°C mark. In other words, a reasonably extended plastic range or "flat" type dilatation curve has been achieved. The data quoted for a typical ghee above in fact illustrate this effect. It is approximately correct that at the slip point the SFI is about 4 (or dilatation 100). If one imagines a milk ghee or a vegetable ghee whose SFI values are numerically the same as those shown but that each temperature is 2°C higher than those indicated, then this material would still be acceptable when regarded as a shortening and is indeed "softer" than a variety of hydrogenated vegetable oil shortenings in common use in many parts of the world. To avoid having too hard and unworkable a fat in cooler temperatures it would be an advantage to obtain SFI at 15° and 20°C rather lower than those shown for the ghee.

Vegetable ghee must be regarded as a cooking fat or shortening, hence a relatively flat dilatation curve is the requirement. Vegetable ghee is a member of the very wide group of hydrogenated oil shortenings and the same techniques which are widely used in other parts of the world to produce these products apply in general to the production of vegetable ghee also. To be precise, flavour stability is one of the primary considerations, as always, and to achieve this, hydrogenation must be taken far enough to bring the level of the reactive, triple unsaturated linolenic acid down to 2% at most, or even to eliminate it altogether. As with other shortening manufacture in Europe and U.S.A. the temperature of hardening if restrained to about 140°C - instead of the usual 180 - 200°C - for most of the early part of the cycle will favour the long plastic range or flat dilatation curve. It does not favour selectivity in the removal of the linolenic group however, so the practical conditions of temperature have to be a compromise. This by some hydrogenaters in the U.S.A. takes the form of allowing the temperature to rise above 140°C for a brief period towards the end of the hydrogenation cycle.

46. BLENDING

The final texture for many shortenings and vegetable ghee itself can be closely approached by hardening one oil or a mixture of oils, but it is probably more common practice to blend two or three hardened oils of different slip points and levels of SFI so that the contribution each makes to the solid content throughout the temperature range enables a close match to be maintained with the specification. The blending operation allows the producer some room for manoeuvre to achieve this. The different hardened oils may be derived from one or more unhardened oils, e.g. groundnut, cotton, soyabean. One of the components may be a liquid oil, as for instance the 5% sesame which is obligatory in India. This enables the vegetable ghee (vanaspati in this instance) to be detected by means of the Baudouin colour reaction; it also happens to contribute a little - about 2% - to the polyunsaturated fatty acid (PUFA) content of the product. The proposition to increase the level of unhydrogenated vegetable oil in vanaspati (though not necessarily sesame) so as to raise the PUFA content, is being actively considered by Indian scientists among others.

47. BENEFIT OF POLYUNSATURATES

The reasons for making available to consumers dietary fats which have a content of PUFA greater than is provided by many traditional sources of fat - especially those of animal origin - are briefly as follows. In diets of adequate and more than adequate caloric content, where fat rich in saturates provides more than about 30% of the total calories, there is a noticeable increase in the level of cholesterol in the bloodstream. Cholesterol is chiefly carried in the blood in the form of its esters with unsaturated fatty acids. Where it is deposited on the walls of blood vessels as the ester of saturated fatty acids the vessels become partly blocked or restricted and this applies to the aorta of the heart as well as the smaller blood vessels especially the coronaries and cerebrals. Thus the conditions of atherosclerosis and certain heart diseases arise. It is also noticeable that the cholesterol level in the blood of people who are prone to heart attacks is higher than average. By increasing the level of polyunsaturated fatty acids in the diet of such people - and one thinks here of the naturally occurring linoleic acid - the cholesterol level may be reduced, although the proportion of polyunsaturates to saturates (SAFA) in these visible fats of the diet must be considerable if they are to offset the saturated fatty acids in the whole diet. A minimum ratio of PUFA/SAFA of 1.2/1 for dietary fat products has been recommended; some special margarines in Europe and U.S.A. aim at 1.5/1 or higher.

48. ESSENTIAL FATTY ACIDS

It would be an exaggeration and misleading to suggest that the association of saturated fats and high blood cholesterol was the sole cause of the heart disease prevalent in many countries where the diet is adequate or above. Lack of exercise, stress, and heavy smoking are also recognized as potent factors. It may therefore be asked quite reasonably why become concerned to provide polyunsaturates in the diet where these factors are notably absent and the most widespread problem is not to cut down saturated fats but how even to approach a diet adequate in caloric content?

Two reasons present themselves. For the proportion of the population who are fortunate enough to enjoy the adequate diet possibly rich in saturates, as mentioned above, it would be desirable to make available in an attractive form some dietary fat products rich in polyunsaturates to combat atherosclerosis and heart disease. For the many millions whose chief concern is to obtain a diet even adequate in calories it is still important to make available polyunsaturated fatty acids because in so doing particular forms of them are thereby supplied: these are the essential fatty acids, (EFA).

In 1930 Burr & Burr first showed that deficiency in particular fatty acids led to a series of ill effects especially in the development of the young. A whole series of bodily functions appear to depend upon a certain minimum supply. More recently linoleic acid has been recognized as being capable of being converted to arachidonic acid in the human body and this acid in its turn is converted to a class of compounds known as the prostaglandins. The latter are involved in a host of bodily functions such as the efficient functioning of nerve fibres, blood pressure regulation, male fertility, uterine contraction and smooth muscle contraction. Obviously more is now involved than the hypocholesterolaemic effect of PUFA and their relation to heart disease. It seems definite that a deficiency of linoleic acid in the young leads to abnormalities but the results of deficiency are not so clearly visible when adults are the subjects. Whereas the human metabolism is capable of deriving the important arachidonic acid from linoleic acid it is not capable of making linoleic acid for which we are dependent upon our diet. The amounts of EFA which must be present in the diet to overcome deficiency effects is about a quarter of the amount of PUFA needed to counteract SAFA in a rich diet. From the data given below it will be readily apparent that much of the PUFA present in the vegetable oils concerned is present in fact as EFA. This then becomes the most important reason why vegetable oils of this type should be widely available in the diet.

Oil	approximate PUFA	approximate EFA
Groundnut	21	21
Cottonseed	52	51
Soyabean	61	53
Sesame	43	42
Sunflower	63	62
Safflower	72	76

9. STRUCTURE OF EFA

As stated in para 1 three molecules of fatty acid are combined with glycerol to form a triglyceride, i.e. oil or fat. It is conventional for most purposes to commence numbering the carbon atoms in the chain which comprises any particular fatty acid with the carbon atom attached to the glycerol as No. 1 and then upwards to the carbon atom at the other end of the chain which terminates in a CH_3- group. In discussing the structure of the EFA if this procedure is reversed and the carbon of the CH_3- terminal group is numbered 1, certain distinctive features are much more clearly discernible. Not only are EFA cis polyunsaturated fatty acids (trans show little EFA activity), but the location of the double bonds in the chain is evidently important also. The double bonds are not alternate (conjugated) but separated by a methylene group, thus -CH:CH. CH$_2$:CH:CH- etc. Further, in the important EFA the first double bond is located at the sixth carbon atom from the terminal No. 1 carbon atom. The number of carbon atoms from the terminal carbon to the double bond is known as the "End Carbon Chain" (ECC), and indicated by the Greek letter small omega, (w).

Chain length	Double bonds (cis) at	ECC (w)	Fatty acid	
C18	6, 9.	6	linoleic	most important EFA
C18	6, 9, 12.	6	gamma linolenic	
C20	6, 9, 12, 15	6	arachidonic	
C18	3, 6, 9.	3	linolenic	less important EFA
C20	6, 9.	6	cis, cis, 6, 9 eicosa decenoic	

Other polyunsaturated fatty acids including some which occur in fish oils show slight EFA activity.

50. GRAIN

After the discussion of the nutritional value of vegetable ghee it is next necessary to consider how it may be made most attractive in appearance from the often traditional viewpoint of different consumers.

When cooled, solid vegetable ghee is a creamy off white if no colouring material has been added. Consumers may expect a very fine smooth grained fat in which case rapid cooling is what is needed. This may even be achieved by merely chilling the oil in the first (A) unit of a votator and filling the super cooled liquid into containers when the fine crystals or grains grow within 24 hours, whilst the temperature is maintained below the melting point.

Where a larger grain is required the same freedom to chill rapidly is not open to the manufacturer. The traditional method has for long been to fill tins with oil at about 10°C above the melting point which is a generally a convenient temperature at which to handle a hardened fat. A temperature of 50°C would be suitable. The tins are then passed into a nearby cooling room where they are stacked in rows across the room several tins high to the convenience of the operator who is doing this by hand. Smaller tins (0.5 Kg. say) may be placed quite close together since for their weight they possess a relatively generous amount of surface from which to radiate heat. Larger tins (15.0 Kg.) must be spaced a little more openly with a few cms. between them. At first the circulation of the external air into the cooling room is adequate to bring down the temperature steadily to the melting point in a few hours, after which the air blown in must be itself cooled (15 - 20°C). As the vegetable ghee cools steadily below its melting point crystals grow and liberate heat so that the temperature now tends to remain steady for up to ten hours after which it continues to fall again for some further hours until about $25^{\circ}C$ is reached. The room may then be emptied. The process is time-consuming and simple. Two to three days may may be taken up by one cycle. With large tins of 2 Kg. and more an area of 100 m^2 will easily yield 150 tons cooled product in the working week, but with smaller tins of say 1 Kg. the output is about half and for 0.5 Kg. tins about a quarter. Anything which shortens the cooling cycle whilst allowing the requisite grain size to appear, naturally enhances productivity.

By immersing the probe of a temperature recorder into a tin of vegetable ghee a cooling curve may be obtained which indicates the initial rate of fall, the period when the evolution of latent heat of crystallization arrests this, and then the final descent to the end of the cooling cycle. Cooling curves which lie above the one described should yield larger grains (slower cooling) and possibly some separated liquid, whilst curves below yield finer grains (quicker cooling) and a close, firm product. It is inevitable that tins on the outside and at the centre of a stack will often show some difference in grain size. If the product is allowed to melt in transit and recrystallize again a different texture may well result. It is interesting to reflect that whether the product is fine or coarse grained in the tin, the first operation by the consumer may well be to melt the vegetable ghee as part of some cooking operations.

51. VITAMINS, COLOUR, FLAVOURS

Just as margarine has been vitaminised now for nearly fifty years it has become general practice to add to vegetable ghee vitamin A to the level of at least 25 International Units per gramme and national legislation may require this to be added in some standard synthetic form. Vitamin D (calciferol) if added will be present at about 3.1 U. per gram. Of the three isomeric forms of carotene the β form is the most potent since the body is capable of splitting one molecule of β carotene to give two molecules of vitamin A. Being responsible for the natural colour of butter carotene is of course an obvious choice for the colouring of margarine or vegetable ghee. If the required level of vitamin A is all added in the form of carotene too intense a colour may be imparted to the product. One way around this difficulty is to add carotene up to the level of the colour required and then make up to the required vitamin A level by the addition of vitamin A itself. In such an event about one third only of the vitamin A will come from the carotene. Ready made mixtures are put on the market. If on the other hand vitamin A alone is used colour can be provided by substances such as annatto, the well known orange yellow pigment extracted from the seeds of Bixa orellana. Synthetic colours which have been used in the margarine industry are also available. Benzene azo-β-naphthylamine (yellow) and o-toluene azo-β-naphthylamine (yellow - red) listed in U.S.A. as Food, Drug and Colour Act yellow Nos. 3 and 4 respectively, are two of the best known and whether used seperately or mixed the level of addition would be about 25 p.p.m.

In the past flavours derived from soured milk and cheese according to local taste have been used by manufacturers of vegetable ghee. Synthetic flavours such as diacetyl used at low levels of 1 or 2 p.p.m. simplify the problem of maintaining a consistent flavour. Other well tried flavours are butyric acid and pineapple essence.

Government legislation may touch upon the oils which are permitted for use in the production of vegetable ghee, the characteristics of the product such as minimum and maximum slip melting points, maximum f.f.a., inclusion of a tracer oil such as sesame and the vitamin level required if any. Added colour, flavour, anti-oxidants, may be prohibited or restricted to certain classes of additive. Manufacturers and exporters must consult these rules.

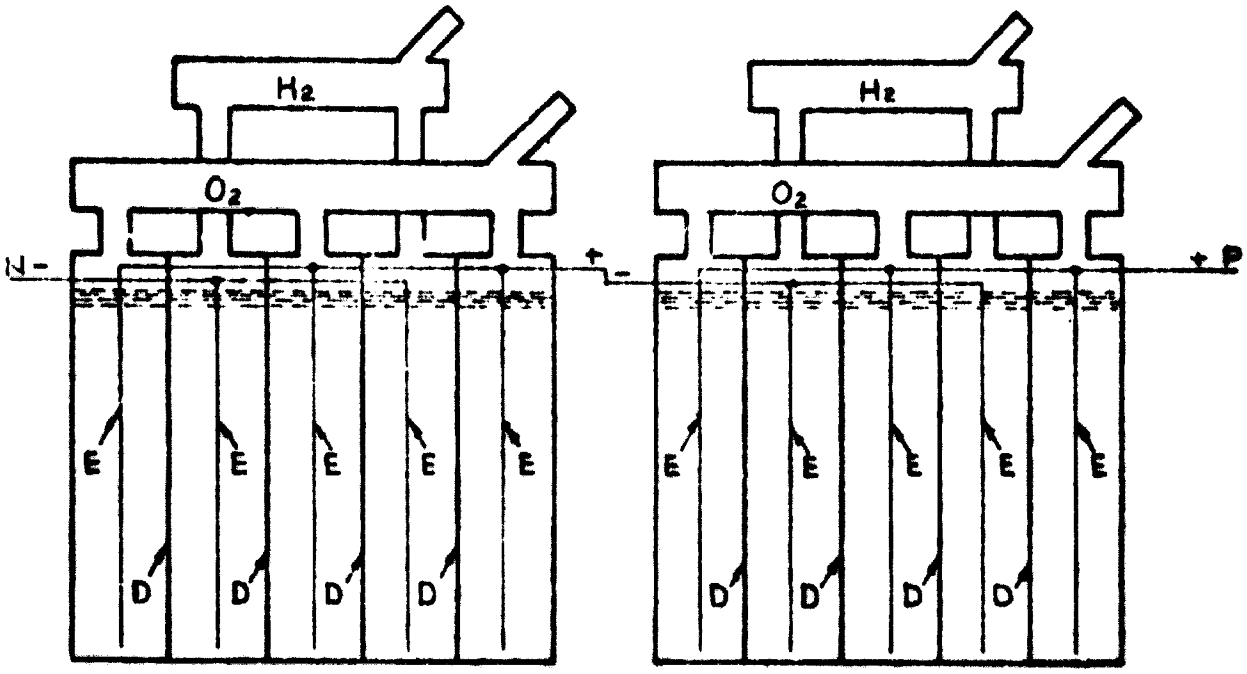
52. PACKAGING

Vegetable ghee is normally packed in tins which have certain obvious merits as containers. Firstly they are robust and withstand transport and frequent handling; secondly their closure is most satisfactory for resisting ingress of air, moisture etc. which could lead to staleness and rancidity developing in the product; thirdly the tin plate can first be printed and then transported as sheets to the vegetable ghee factory for making up into tins upon a simple machine immediately prior to being filled.

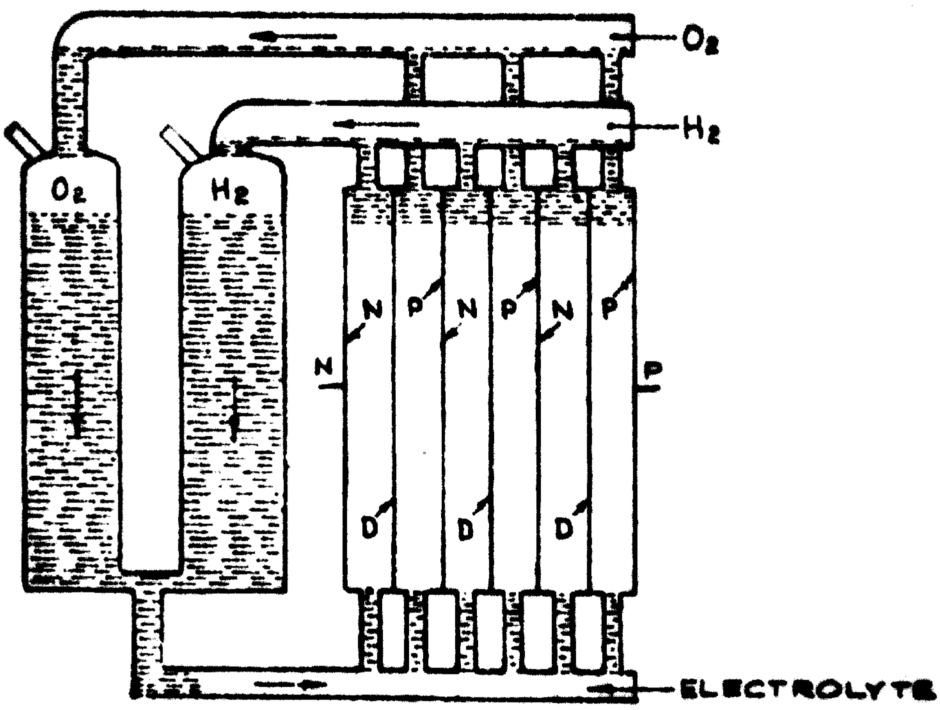
Plastics such as high density polythene, high density polypropylene and polyvinyl chloride may prove sufficiently robust to act as containers depending upon conditions of distribution. In difficult distribution conditions where the temperature may rise above the melting point at times and where a shelf life up to a few months is needed, a metal foil insert sealed over the surface of the product in the container is necessary. This keeps air out and melted liquid in. It must be decided whether it is most economic to assemble the plastic containers on site - injection moulding or thermo forming - or whether to transport them in bulk already fabricated.

BASIC DIFFERENCE BETWEEN UNI-POLAR AND BI-POLAR CELL ARRANGEMENT.

APPENDIX 1

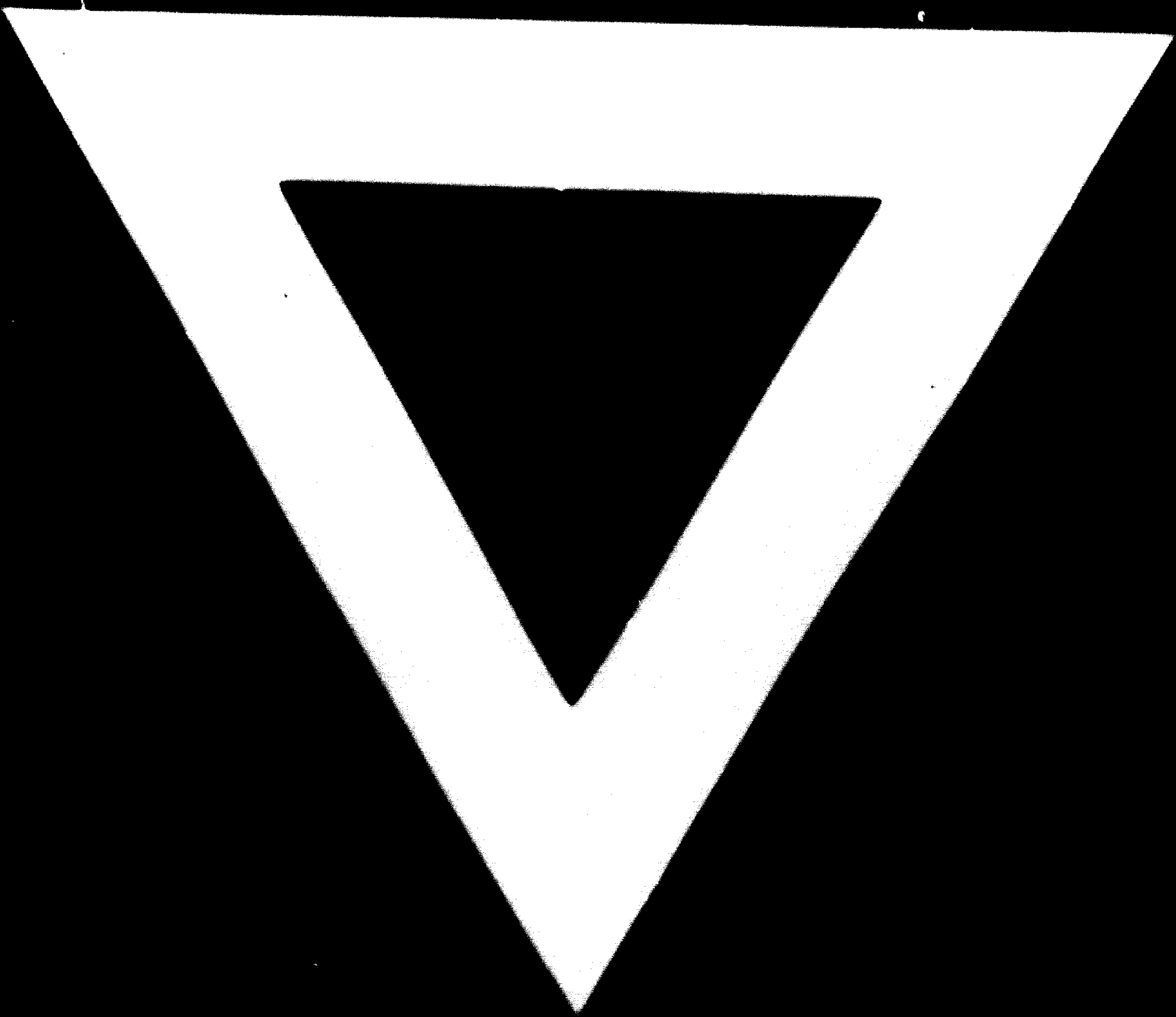


(a) UNI-POLAR CELL



(b) BI-POLAR CELLS.

D - DIAPHRAGMS.
E - ELECTRODES.
P - POSITIVE POLE.
N - NEGATIVE POLE.



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