Continuous Hydrogenation In The Oil Hardening Industry

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THIS article should under no circumstances be looked upon as an attempt to contribute anything original or new on the subject of continuous hydrogenation of oils, but merely as an endeavour to sum up the available data and information in this field in the light of the author's personal experience.

As far back as 1897 Sabatier and Senderens showed that many ethylenic organic compounds combined with hydrogen could be converted into the corresponding saturated derivates, if exposed in the state of vapour to the action of a number of reduced metals, amongst them, for instance, nickel. Sabatier found that oleic acid vapour could thus be converted into stearic acid.

In 1902 Norman found that nickel exhibited a catalytic effect not only when the hydrogenation was conducted in a vapour phase, but also in a liquid surrounding. This discovery can be truly regarded as the foundation stone of the oil-hardening industry.

Since then a number of methods for commercialising the hydrogenation process have been evolved, and something like 300 patents have been granted, most of them, however, based on Norman's original master patent.

The hardening of vegetable and marine oils has become today an industry of impressive importance. Before 1914 this industry was mostly confined to the manufacture of fats of technical qualities for candle and soap making. The Great War, by stimulating the demands for butter and fat substitutes, has been primarily responsible for the fact that huge quantities of oils are being hardened today for edible purposes.

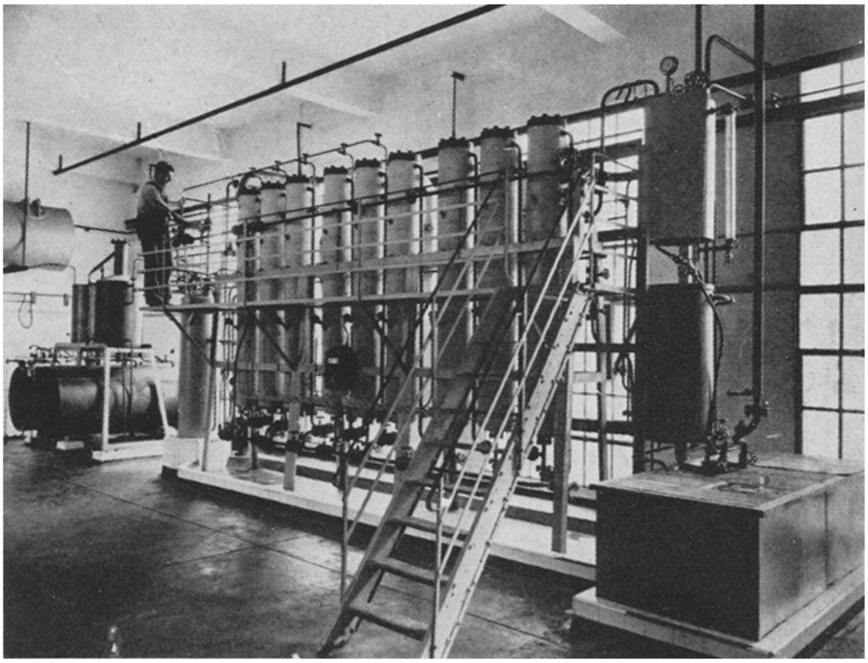
The margarine, confectionery, and other not less important industries, are the main consumers of edible fats at the moment. Something like 500,000 tons of whale oil alone were converted into hard fats in 1935, to say nothing of the huge quantities of sunflower oil, ground nut oil, cotton oil, etc., which are being converted into margarine, lard compounds, etc.

So as to be able to draw a parallel between the prevailing hardening methods and the continuous process, I will here give a short survey of the various processes applied in the industry and developed in the course of recent years, during which the oil hardening industry has been going through various degrees of development.

Hydrogenated oils produced in the initial stages could not claim in any way to be equal to natural fats. Only for the last twenty years have homogenously hardened fats been produced successfully. These fats hardly differ from natural fats, except for certain peculiarities of their glyceride structure.

Before turning to the description of the hardening methods, I would like to say a few words on the paramount importance of the prerefining of oils irrespective of the methods employed. This cannot be over-emphasised. There is always a larger or smaller amount of organic sulphur compounds, oxi-fatty acids, albuminous matter, traces of phosphorus containing lecithin, etc., present in the crude oil. All these interfere more or less with the hardening process. They exercise a toxic effect on the catalyst, thus reducing its catalytic usefulness and rendering the catalyst prematurely inactive. The formation in crude marine oils of formaldehyde, which is again a very powerful toxic agent, has also been observed. Moisture should also be avoided, as far as this is possible, by taking ordinary precautions. though it is not essential for rigidly anhydrous conditions of the oil to be maintained. As already stated, owing to their absorption by the nickel catalyst in preference to that of the fatty compounds, all these impurities should be eliminated as completely as possible.

It is the general practice to remove the free fatty acids and other undesirable impurities by a neutralising process to which caustic soda of various concentratons is applied. Quite recently a new method of neutralising has been



A Nine-Tube Hardening Plant.

developed, viz., the removal of free fatty acid by the Wecker process, by which neutralisation is accomplished not by means of adding lye, but by distilling the free acids with steam. While, in my opinion, it is very difficult to remove the whole bulk of free acidity by applying this method, its application in cases where a high percentage of free fatty acid is present in the oil, is worth consideration. This does not, however, exclude the necessity for applying the old conventional method in cases where the total free fatty acid content has to be reduced to say 0.1%.

Deodorisation of the crude oil as a part of the pre-refining, before the actual hardening, is often a desirable feature in cases such as coconut or palm kernel oil.

As a result of theoretical research and the considerable amount of data contributed by workers such as Sabatier, Senderens, Norman, Erdmann, Bedford, Wilbuschewitz, Goldschmidt, Lush, Bolton, Williams and others, two distinct methods can be traced as being applied today in the industry dealing with the conversion of liquid oils into a hardened form, although one must admit that there is no very clear line of demarcation between them.

Of these two methods, (A) is that generally known as the Batch Process, and the other (B), which has recently come into prominence, is the T.R.W. Continuous Process.

These methods, which are somewhat of a complex nature, necessitate the following operations:-

(a) Preparation of the oil before the hardening takes place;
(b) Production of the catalyst;
(c) Manufacture of the required hydrogen, which is mostly done by electrolysis. Less frequently it is produced by passing steam over red-hot metallic iron. This, however, results in a hydrogen of an inferior quality to that produced by the electrolytic method.
(d) Actual hardening of the oil;
(e) Recovery of the catalyst;
(f) After-treatment of the hydrogenated oil.

The final operation, in the case of the Batch process, consists of the neutralising, washing, bleaching, and deodorising of the fat. In the case of the T.R.W. process, for the reasons given below the after-treatment of the oil is limited to deodorising only.

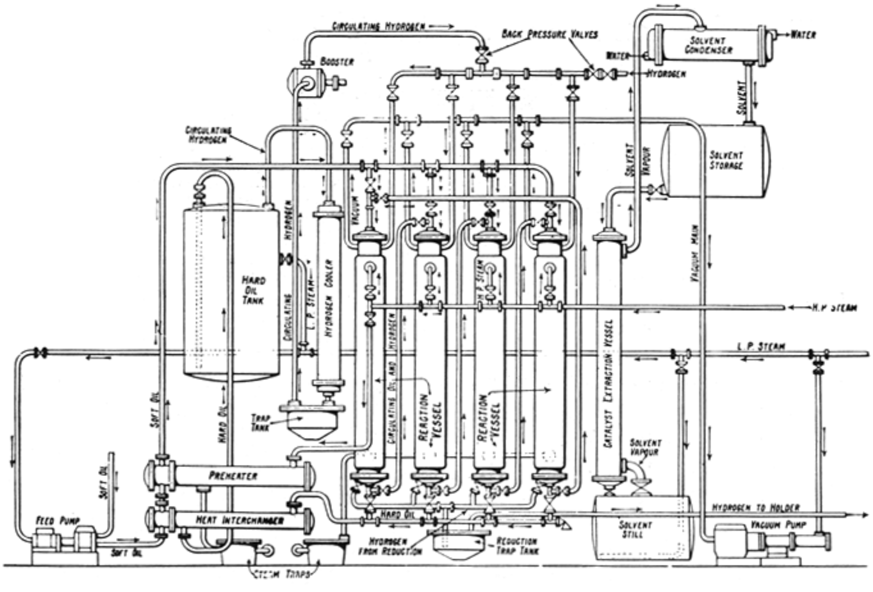


Fig. 10.—Layout of Complete Plant for Hydrogenating 25-50 Tons of Oil per week

(A) Since the first Norman patent, based on the principle that fatty acids could be reduced by hydrogen in the presence of a nickel catalyst, discovered in the laboratory of Sabatier, there have been many minor modifications and improvements in the original process. However, in the main the general practice for the Batch process remains the same, viz. the preparation of nickel salt with or without a support, its reduction in hydrogen at a temperature of 300°C. to 350°C. to metallic nickel, the addition of the finely divided catalyst to the oil, and the mechanical agitation of both with hydrogen at about 180-220°C. for the necessary time, very often for some hours. Various means have been introduced to increase the contact between oil, gas and catalyst, but the reaction, including the period of heating and cooling down of the oil, still takes a considerable time.

The batch process can be conducted by using a nickel catalyst with or without an inert support. In the first case, the catalyst is, so to speak, attached to a support, generally kieselguhr. In the second case, the catalyst is free and suspended in the oil. The second case is typically represented by the nickel formate method. This catalyst is produced by breaking up the nickel formate in a vacuum or inert gas at a temperature varying between 200-230°C. according to the following equation —

$$Ni(HCOO)2 = Ni + 2H + 2CO_2$$

This process can also be adopted in a surrounding of oil, which will protect the nickel dust from oxidation.

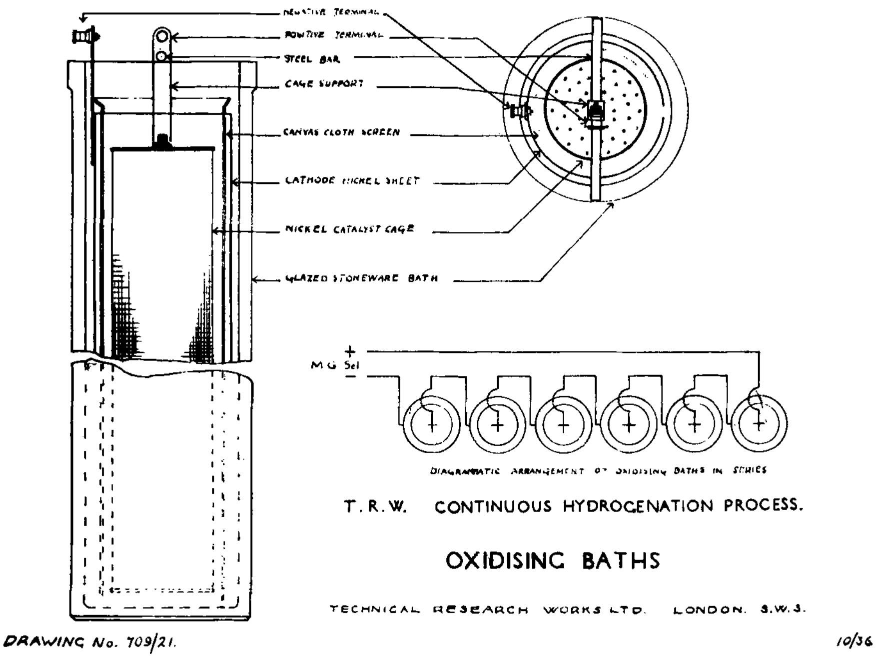
From a mechanical point of view the Batch process can be subdivided into

1. the Norman method, in which mechanical agitation is used to effect an intimate mixing of three elements which are essential to produce the desired hardening effect, viz. oil, catalyst and hydrogen.
2. the Wilbuschewitz method, in which mixture of the oil and catalyst is constantly injected as an atomised spray into a chamber filled with hydrogen by means of a specially designed pump.

As can be seen, the object of the two methods is to effect intimate contact between the oil, the catalyst and the hydrogen.

The disadvantages inseparable from the use of any batch process may be summarised as follows:-

1. The preparation of powder catalyst is costly in respect of both the labour involved and the plant required.
2. As the catalyst is warming up to its work the process must be stopped because the particular charge of oil has been sufficiently hydrogenated.
3. The reactivation of spent catalyst involves several operations and is costly in plant and labour. Only comparatively large factories can recover the catalyst on an economic basis, thus giving an unfair advantage to the large manufacturer.
4. The production of nickel formate, if and when used as a catalyst, is not an economic



proposition unless manufactured in large quantities. This fact has even been admitted by its inventors.

5. Oil, especially of the semi-drying type, such as cotton oil, deteriorates in colour and flavour by prolonged heating.
6. The hydrogenated oil must be separated from the suspended catalyst powder by filtration. This involves certain manufacturing losses.
7. There is an inevitable formation of free fatty acid, so that the hardened product has to be soda refined after hydrogenation, if it is to be used for edible purposes.

(B) This brings us to the T.R.W. Continuous Process, the description of which is the main object of this contribution.

It goes without saying that any continuous hardening processes on an industrial scale, avoiding the use of a catalyst powder with or without an inert support and obviating the necessity of filtration, must be considered of the greatest value to the industry. Such claims were made by Bolton in 1919, and one may say that he and his co-workers, as the originators of continuous hydrogenation are undoubtedly entitled to recognition for having brought us closer to the principle of continuity in an industrial field, the functions of which are becoming more important every day.

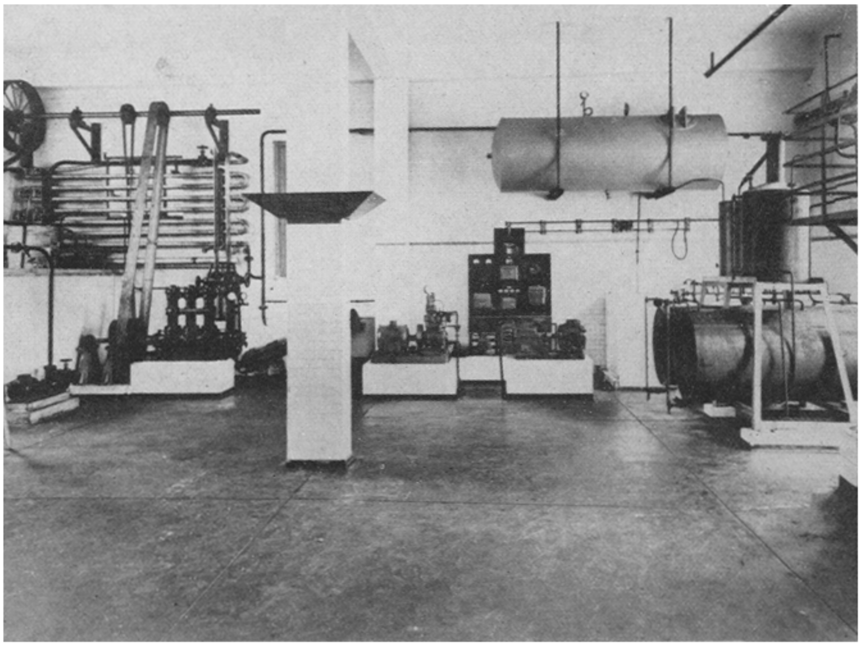
According to Bolton's original invention, an oil flowing through a stationary nickel catalyst could be converted into hydrogenated fat and withdrawn from the installation continuously, thus establishing the principle of continuity for the first time in the history of hydrogenation.

With this new process, Bolton claimed that hydrogenation is governed by the effect of temperature, pressure, mass of catalyst, and flow of oil. As can be noticed the effect of agitation, which plays an important part in the batch process, has been completely eliminated.

Following this development, a patent specification was filed by Technical Research Works Ltd. and Lush, introducing an improved method of activating and reactivating the metallic catalyst. The inventors claimed a novel feature for activating and reactivating the nickel catalyst by using the catalyst cage as the anode in an electrolytic bath. At this stage I would like to point out briefly the essential difference between the two methods.

The fundamental idea underlying the T.R.W. Continuous process is that a solid stationary catalyst is placed in a battery of drawn steel, jacketted hollow columns about 7′ long and 6″ in diameter. The catalyst, commonly known as catalyst cage, consists of monel metal gauze filled with activated pure nickel turnings. Each of the columns holds two cages, each 3′6″ in length and 6″ in diameter. Oil and hydrogen pass through the catalyst, under appropriate pressure and temperature conditions, and the oil undergoes the hardening process whilst flowing through the system of catalyst cages. Having passed the series of columns it is freed from an excess of hydrogen, cooled and conveyed to an appropriate storing vessel.

As already mentioned, however, the important feature of the T.R.W. continuous process is the method of preparing the catalyst and its reactivation after its catalytic properties are spent as a result of its gradual poisoning in the course of hydrogenation.



In the foreground can be seen the Motor Generators and in the right-hand corner the Activating Installation.

The complete process consists of the following cycle of operations:-

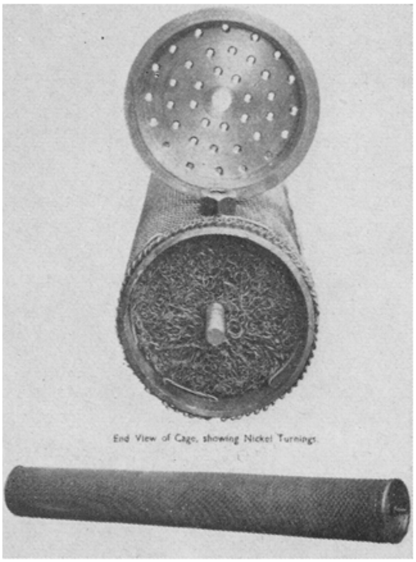
1. The preparation of the catalyst, a process which comprises anodic oxidation of the catalyst in an electrolytic solution under the following operations:-

   The catalyst cage is made and the anode in an electrolytic bath. Earthenware pots are generally used for this purpose with nickel sheet cathodes fitted inside forming the cathodes. For the standard cage the maximum current strength required is only 40 amperes at 4 volts for each cage for a period of 36 to 48 hours.

   The electrolyte in the bath consists of a very dilute solution of sodium carbonate. As the result of the oxidation a thin film is evenly formed over the surface of the catalyst. Such a thin film is generally easily reduced to metallic nickel and the resulting catalyst is extraordinarily active. After the surface of the catalyst has been covered by a film of black nickel oxide (the estimated thickness of the active film is 0.0003 mm.), the cages are washed in distilled water until the water used for that purpose shows no traces of carbonate.

   The initial cost of the stationary catalyst is fully offset by the cost of the nickel powder catalyst, which is estimated to be between 50 c. and 70 c. per lb.; the loss of powder catalyst in the hydrogenation process under the most economic conditions is 0.1% of the oil hardened; in some cases it is reported to be as high as 0.2%.
2. Following oxidation, the reduction of the nickel oxide to metalic nickel takes place. The catalytic cages are removed from the oxidation bath, washed as described above, and placed in the hydrogenation columns. The reduction of the nickel oxide is achieved by passing hydrogen gas under slight pressure through the catalyst cages at a temperature of about 250°C.

   $NiO + H_2 \rightarrow Ni + H_2O$
3. The actual hydrogenation occurs when the preheated oil and hydrogen are introduced under pressure varying between 50 and 150 lbs. through the system of the activated catalysts.
4. After the catalytic properties of the cages have been spent the catalyst cages in the columns undergo a degreasing process, in order to prepare the surface for the succeeding reactivation. This is achieved by pumping a solvent through the installation.



Catalyst Cage

   The solvent can be recovered by distillation in the usual way.
5. Following the degreasing, reactivation of the catalyst cages, to restore their activity, as described in paragraph 1, takes place.

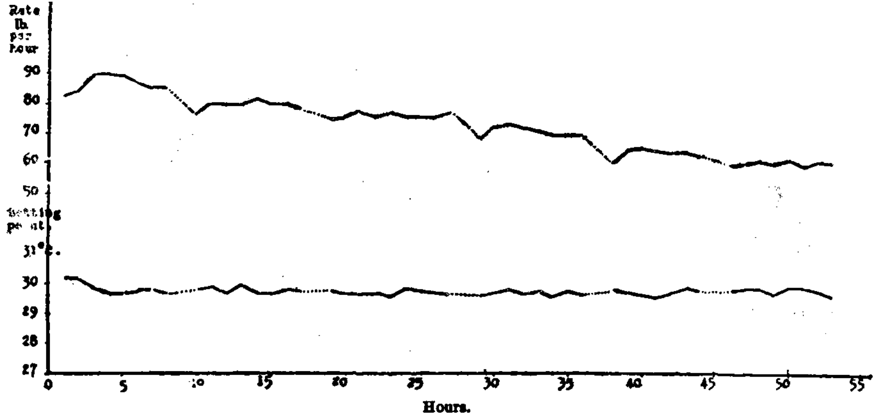
The advantages of the continuous process, as confirmed by the data obtained by the author from his practical experience, are:

1. Continuity of operation.
2. The catalyst may be regarded as part of the plant and can easily be reactivated for years without any appreciable loss.
3. A fairly easy control of the composition of the hydrogenated product (selection) and the maintenance of a constant homogeneous quality.
4. The output of the plant is inversely proportionate to the extent of hydrogenation.
5. There is no formation of free fatty acid; consequently a neutralisation of the hardened fat becomes superfluous.
6. The filtering of the oil due to the absence of powdered catalyst is eliminated and no filtering losses are sustained.
7. It admits slight hydrogenation on an economical basis. This is a very important factor for the hydrogenation of oils with a low iodine value.
8. The time required for the action of the heat on the oil is short; therefore no discolouration or the appearance of the characteristic hydrogenation smell takes place.
9. It becomes obvious that under the above described conditions the manufacturing costs of the operations involved are lower.
10. It is a simple installation which does not require a highly qualified engineer to install and run.

Summing up, one may say that the plant is self-contained, the catalyst practically permanent, and very easily and inexpensively revivified. It is interesting to note from the table below how the activities of the catalyst increase after a few runs, when the catalyst, so to speak, begins to "mature."

Extract From a Log Sheet
6″ Tube

Run	Reduction in Iodine Units	Time Required	Production in Kilos
1	28	20 hours	1800
2	25	62 hours	7000
3	20	118 hours	13000
4	26	202 hours	22000
5	24	296 hours	45000



Decrease in activity of catalyst during hydrogenation to constant setting point of palm kernel oil. (The dotted lines indicate the closing down of the plant each night.)

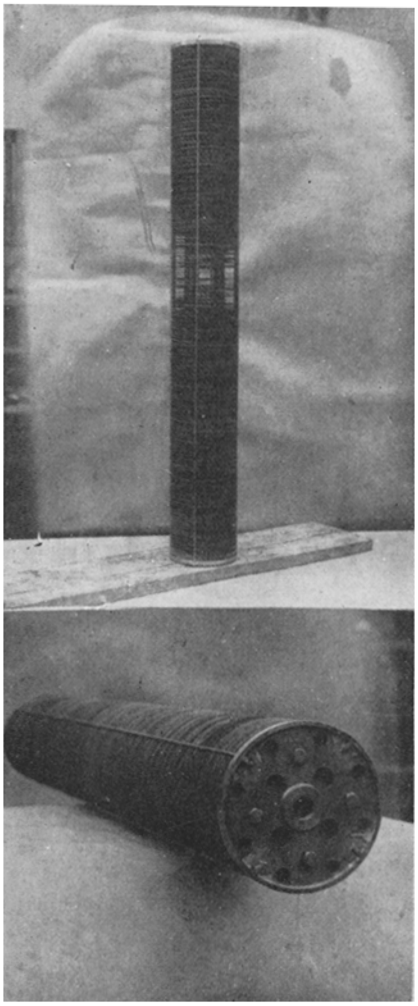
Fig. 1.

The acidity of the oil before hydrogenation, expressed in oleic acid, was .08, while after the hardening took place, this increased to .11 — a very negligible increase in acidity.

Relation between iodine value and time for an actual hydrogenating period of 312 hrs. Cottonseed oil used—iodine value 107.

Fig. 2

No time is spent in charging and discharging large reaction vessels, nor in filtration, and in most cases the desired degree of reduction in iodine value is easily obtained by altering the speed of flow of the oil so that the output can be a large one when only slight hydrogenation is required. It can be said that the continuous process, as developed by Bolton and Lush, has largely solved the slight hydrogenation which is often used for bleaching purposes. For instance, the bleaching of palm oil by a slight hydrogenation can be made a paying proposition by applying the T.R.W. process. By a reduction of 2 to 3 iodine units the author succeeded in obtaining a very satisfactory change of colour in palm oil. The carotene, which is mainly responsible for the orange yellow coloration of the palm oil, has previously been reduced before the hardening had any effect on the other unsaturated fatty acids.



The New Catalyst consisting of Perforated Nickel Discs.

The method of maintaining a uniform composition and keeping the process under rigid control is simple. How easily a uniform melting point can be maintained, irrespective of the activity of the catalyst, can be seen from Fig. 1. (Journal of the Society of Chemical Industry — December 2nd, 1927). It is desired to manufacture a hardened oil having a setting point of 29.5° C. to 30° C.; this object is achieved by slightly decreasing the rate of flow of the oil to the necessary extent, as shown by the top line, to compensate for the reduction in activity of the catalyst brought about by use. In this way a constant setting point is definitely maintained, as shown by the bottom line. It will be noted that when the plant is shut down at night, as indicated by the dotted lines, a drop in activity results, showing that continuous working is desirable. This illustrates in a way the advantages of the continuous process over the batch process.

Another method of control is illustrated by Fig. 2 prepared by Appleyard of the British Oil & Cake Mills, Ltd. with an earlier type of plant. In this case the flow of oil is kept constant and a definite iodine value is maintained by modifying the temperature. The influence of each additional pot (column) is shown, and also the necessity of having not less than 3 or 4 of them in series.

When a new pot is put into the series the temperature is dropped and slowly raised to balance the fall in activity of the catalyst, so as to maintain a constant iodine value.

The author's experience bears out the claim of the manufacturers of the T.R.W. plant, that a fairly constant iodine value can be maintained by an intelligent manipulation of temperature, hydrogen pressure and flow of oil, to offset the decreasing activity of the catalyst.

In some cases there are certain objections from a practical point of view to the presence of iso-oleic acid in fat compounds. This is not so much because of their higher melting point but by reason of the crystal structure of the solid iso-oleins, which tends to affect the appearance and consistency of the edible fats in which they may be present.

Another objectionable property of these acids is connected with their behaviour as soap, partly due to their lower solubility and much higher surface tension than of soaps prepared from oleic acid. They also possess a much lower lathering property than soaps made from natural fatty acids of the same degree of unsaturation. On some occasions, however, a larger percentage of iso-oleic acid is desirable as it produces a more homogeneous product.

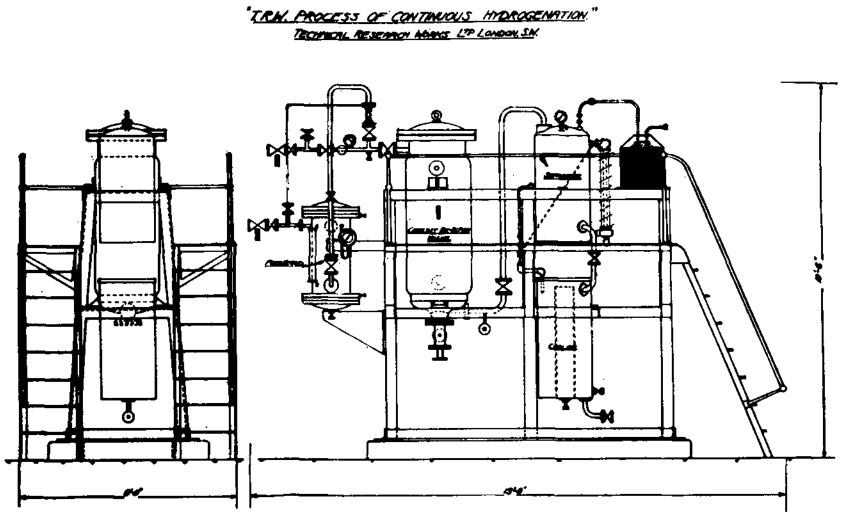
It may be interesting to point out that the T.R.W. process lends itself exceedingly well to regulating the proportion of iso-oleins in the fat, by using one of the two operating methods described below.

Hardening by the continuous process may be conducted in two different ways which result in two different products — (a) what is generally called in practice the overflow method, when the tubes are filled up to their utmost capacity and the oil is allowed to overflow at a certain rate; (b) the other method is known as the drip method, when the oil is allowed to drip down the catalytic cage at a certain regulated speed. It is interesting to note Lush's observations that very little difference is shown in the rate of hydrogen absorption by the two methods. It has however been noticed that the overflow method produces an oil with a higher melting point for a given iodine value. The difference in physical condition resulting from the application of the two methods led to the interesting discovery that the overflow method gives a conversion of linolic acid to iso-oleic and stearic acid. The drip method, on the other hand, shows as the main change the conversion of linolic acid to stearic acid with only a small percentage of iso-oleic acid.

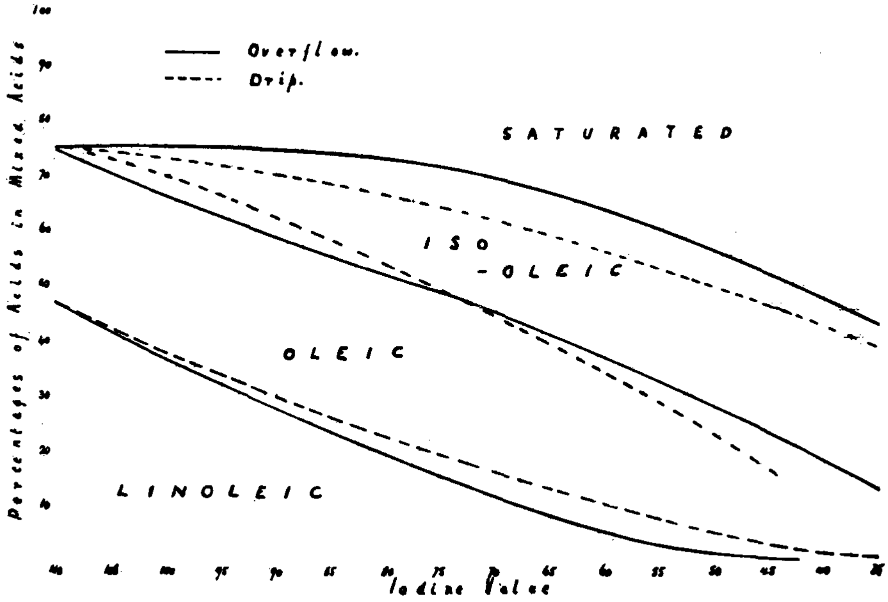
The graph below has kindly been placed at my disposal by Mr. H. R. Mitchell, Managing Director of Technical Research Works, Ltd.

In conclusion, I would like to say a few words of constructive criticism about the plant as it stands today. This is without any intention to minimise the value of the plant to the oil-hardening industry.

In my considered opinion the present T.R.W. plant should be regarded as a workable installation to treat say 20-30 tons of oil per day. It would have certain limitations if the production of larger quantities came into question. The makers of the T.R.W. plant maintain that the present sized catalyst is essential for the satisfactory working of the plant and consider it inadvisable to increase the size of the catalyst and consequently the size of the column, thus limiting its output. In view of this, it would be very difficult to imagine the simple working of a plant, consisting of something like 360 columns, for the production of say 200 tons of ground-nut oil to be hardened to a melting point of 40° C.



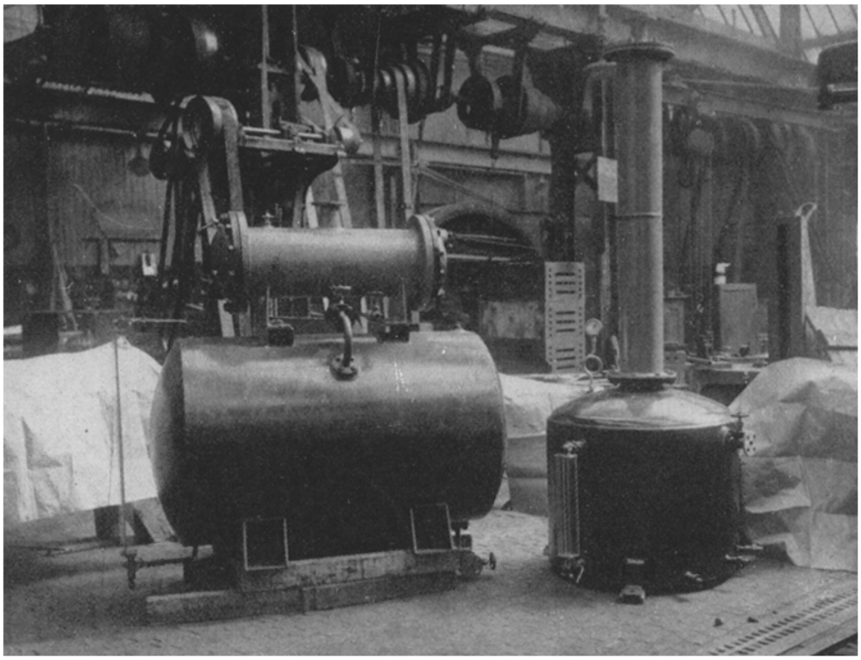
Schematic Drawing of the new T. R. W. Plant.



COMPOSITION OF HYDROGENATED COTTON SEED OIL.

The T.R.W. process, while retaining its basic features should, in my opinion, undergo a substantial reconstruction, which would enhance its value when treating larger quantities of oil. This reconstruction should lead to a further simplification of the various operations involved. The present system of heating the plant is very far from being perfect, and an improved heat interchange would increase the general efficiency of the plant. Furthermore, although the mass of catalyst which takes part in the process is, in the opinion of the inventor, the most important factor, the increase of the catalytic surface exposed to contact with the oil and hydrogen would, in my view, have a beneficial effect in prolonging the life of the catalyst. The present method of using nickel shavings tightly packed in the cage, is not, I may say, the best way of obtaining the maximum active catalytic surface. The degreasing of the catalyst which follows the hardening process, when the catalytic properties are spent, could also be improved in order to achieve the complete removal of the smallest particles of fat in the catalyst; this for obvious reasons, as the anodic oxidation which follows the degreasing cannot fulfill its function of converting the nickel into nickel oxide when the nickel surface is covered with oil. An increased oxidised surface would result, and this in its turn would lead to a larger area of reactivated nickel in the regenerating operation. A further attempt should be made to decrease the sensitivity of the catalyst towards various toxic agents, particular attention being paid in this respect to its sensitivity towards the free fatty acids, although an opinion has been expressed that the presence of the free fatty acid actually does not hinder the hydrogenation. The better results obtained in the hydrogenation by the pre-refining of the oil is attributed to the removal of the various impurities present in the crude oil which are eliminated by the neutralisation of the oil as a part of the pre-refining process. A minute investigation of the effect of the various toxins in the life of the catalyst would, in my opinion, be warranted.

At the present time, when the knowledge of vitamins is throwing more light on their importance in our everyday life, it is not uninteresting to compare the effect which



The Improved Degreasing Installation with Redesigned Still for recovery of the spent solvent.

the two hardening methods (Batch and T.R.W.) have on their preservation in the oil. It is known how sparing nature has been so far as vitamin contents in the vegetable oils are concerned, and how important it is to retain the vitamin content in such oils which possess this advantage. There is sufficient evidence available that commercially hardened oils appear to lose their vitamins in the process of manufacture. It is presumed that this is not due to hydrogenation per se but mostly to other conditions, such as high temperature, an opinion which has also been expressed by Hilditch. The vitamins A and D hardened by Dubin and Funk under vacuum appear to be unaffected by the treatment. The same applies to wheat germ oil where hardening at low temperature has been effected without any injury to vitamin E. The author undertook some research in this direction and obtained evidence that palm oil hardened by the T.R.W. process has retained its vitamin content to a much greater degree than the same oil treated by the Batch process. The possible explanation of this is that the time during which the oil comes in contact with heat and catalyst is limited from 10 to 20 minutes. This particularly applies to hardening by the batch process when nickel formate is used as catalyst which requires a temperature varying between 200° C. and 220° C. Without any fear of contradiction one may say that the vitamin content of oil, which has been hydrogenated at a temperature above 150° C. for some length of time, as required in the Batch process, is usually almost deficient in vitamins.

The continuous process opens up new possibilities not only in the hardening of oils, but also in hydrogenation of chemicals, some of which are dangerous to handle — such as phenol; others require strict temperature control, such as aldehydes, while some of them are very sensitive to reduced nickel oxide, such as furfurol. Phenol, cresol, napthalene, pyridine, and croton aldehyde, are already being hydrogenated. In each of these cases a film of reduced nickel oxide on a nickel surface used in a continuous process approaches the ideal of simplicity and safety.

The T.R.W. plant, of a standard type, has been successfully used by an important oil company in England to produce iso-octaine from di-isobutylene. This plant is operating on a semi-commercial scale, the reaction of the hydrogenation of the di-isobutylene taking place in a vapour phase.

While this short contributation was in course of preparation it came to the author's knowledge, by the courtesy of T.R.W. Ltd., that an entirely new modification of the present hardening plant is about to be adopted. From the schematic drawing given below, it can be seen that the multitubular plant has been replaced by a single reaction vessel which contains an appropriately shaped catalyst. The catalyst cage has also undergone a radical change. The nickel shavings have been replaced by nickel discs, finely perforated. The heating of the new installation is effected by circulating preheated mineral oil. The modus operandi has remained the same and the new system, in the same way as the old, permits the hardening of the oil by the overflow or drip method. Without in any way claiming that the critical remarks expressed by me have had any influence on the new design, it is very gratifying indeed to note that the modified installation is aiming to remedy all the weaknesses which, in my opinion, were to be found in the old type.

General view of portion of analytical laboratories of Central Soya Co., Inc., Decatur, Ind.