# Hydrogenation Practice

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## ABSTRACT

This paper deals with such topics as the changes in the molecular dimensions of a triglyceride during hydrogenation and the effect of catalyst structure on selectivity and filterability and the effect of sulfur on activity and isomerization, the prevention of aromatics formation during hydrogenation of highly unsaturated oils, explanation and prevention of green coloration of oil, the effect of phosphatides on selectivity and *trans*-isomer formation. Heat saving equipment and process control are discussed.

## INTRODUCTION

The catalytic chemist who processes natural triglycerides has to cope with severe, and sometimes conflicting demands. For some types of salad oil and margarine products it is necessary to hydrogenate feedstocks whose component fatty acid chains are very unstable (Table I) (1).

**TABLE I**

**Relative Rates of Oxidation of Fatty Acids**

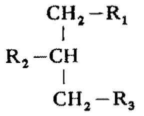
| Fatty acid | Relative oxidation rate |
|---|---|
| Stearic | 1 |
| Oleic | 10 |
| Linoleic | 100 |
| Linolenic | 150 |
| α–Eleostearic (*cis*, Δ9, *trans*, Δ11, *trans*, Δ13) | 800 |

The hydrogenation must be controlled, so that a maximum amount of the linoleic acid chains can be maintained. Other types of products require a hydrogenated triglyceride containing the highest possible content of the *trans*-isomer of oleic acid. In both cases, the formation of fully saturated stearic acid must be prevented, as its presence endows the product with an unpleasant "sandy" taste as a result of the higher melting characteristics of tristearins. This modification of molecular structure is commercially done by hydrogenation and *cis-trans*-isomerization.

Not only is it required to modify the fatty acid chains selectively, but the site of the selective reaction must also be controlled.

In order to produce margarines of a high linoleic acid content, one must distribute different fatty acids randomly over the glycerol molecules. Chemical conversions of the natural products can be qualified as watchmaker's work on a molecular scale. As a consequence, the requirements for selectivity of the catalyst are especially stringent. In addition to high selectivity, the catalyst must possess high activity to combat the effects of many catalyst poisons present in the natural raw materials. To illustrate the requirements of the selectivity we will consider modification in the triglyceride molecule.

When subjected to hydrogenation conditions the shape of the hydrocarbon chains is modified in a stepwise fashion.



$$\begin{array}{l} \quad CH_2-R_1 \\ \quad\ | \\ R_2-CH \\ \quad\ | \\ \quad CH_2-R_3 \end{array}$$

$R_1$ = C18:3 (linolenic = Δ9, Δ12, Δ15, unsaturated)
$R_2$ = C18:2 (linoleic = Δ9, Δ12, unsaturated)
$R_3$ = C18:1 (oleic = Δ9 unsaturated)

**FIG. 1. Model triglyceride.**

Consider the model triglyceride in Figure 1. We can now conceive the hydrogenation as proceeding in a hypothetical manner in 10 separate stages. The hydrogenation reaction is assumed to be selective, implying that as the chain is more unsaturated, the more rapid the hydrogenation takes place. Reaction rates are shown in Table II (2).

Evidence has been published that defines an initial double bond shift to form a conjugated system to be prerequisite for the isomerization reaction, which leads to the formation of *trans*-isomers.

Figure 2 shows an artist's impression of the triglyceride to be hydrogenated to the tristearic acid ester. This is one of the nine conformational possibilities of the molecular structure shown in Figure 3 (3; private communication with B. Beagley).

**TABLE II**

**Relative Hydrogenation Reactivity of Different Fatty Acid Chains**

| Fatty acid chain | Relative hydrogenation reactivity |
|---|---|
| Linolenic (Δ9, Δ12, Δ15) and (Δ6, Δ9, Δ12) | 40 |
| Linoleic (Δ9, Δ12) | 20 |
| Oleic (Δ9) | 1 |

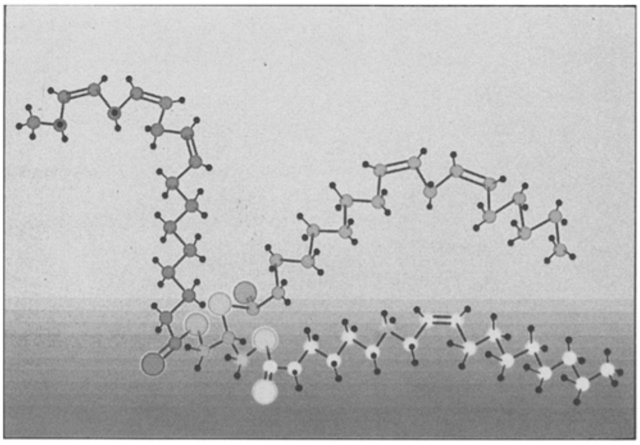


**FIG. 2. Starting triglyceride.**

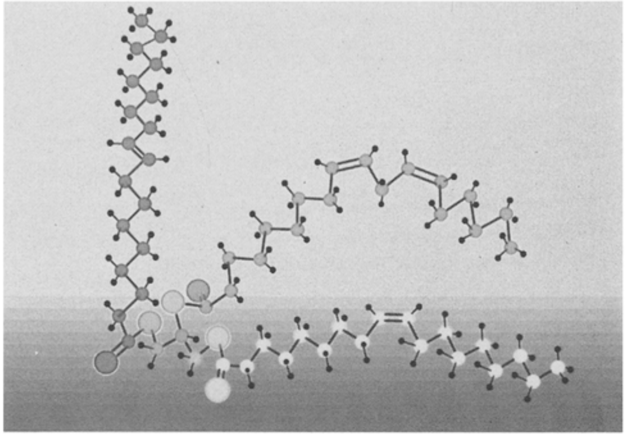


FIG. 7. Hydrogenation of the conjugated C18:2.

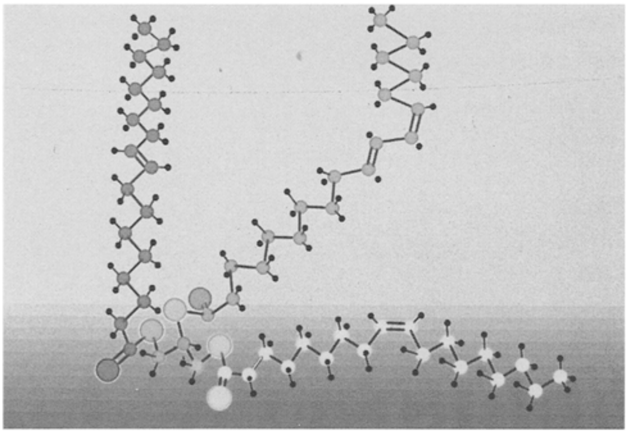


FIG. 8. Conjugation of C18:2.

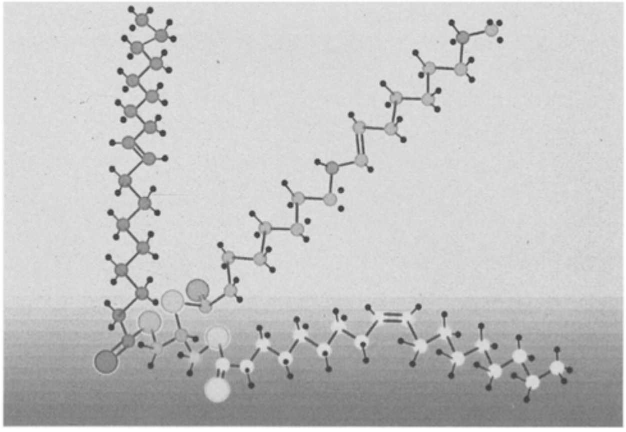


FIG. 9. Hydrogenation of the conjugated C18:2.

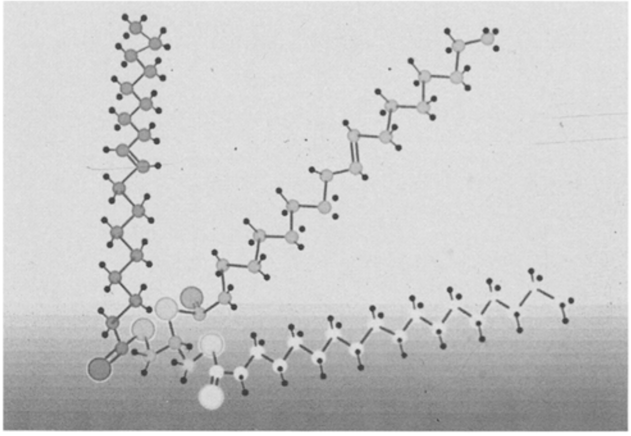


FIG. 10. Hydrogenation of C18:1 Δ9(*cis*).

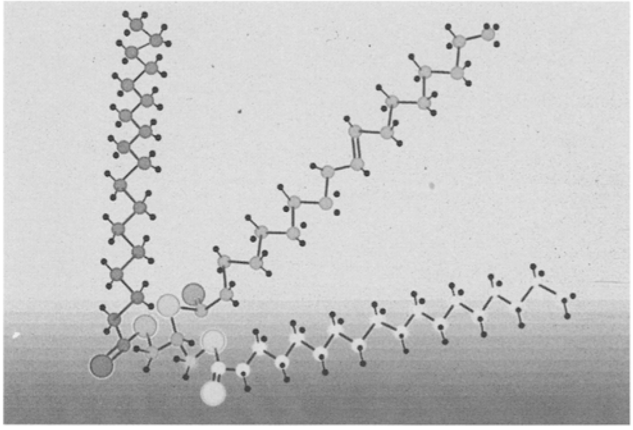


FIG. 11. Hydrogenation of C18:1 Δ9(*trans*).

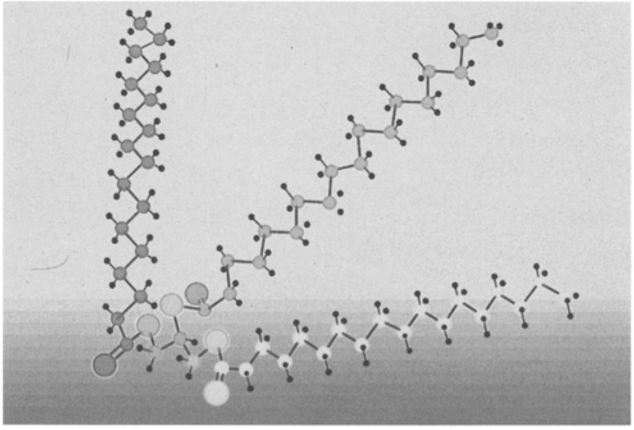


FIG. 12. Hydrogenation of C18:1 Δ10(*trans*).

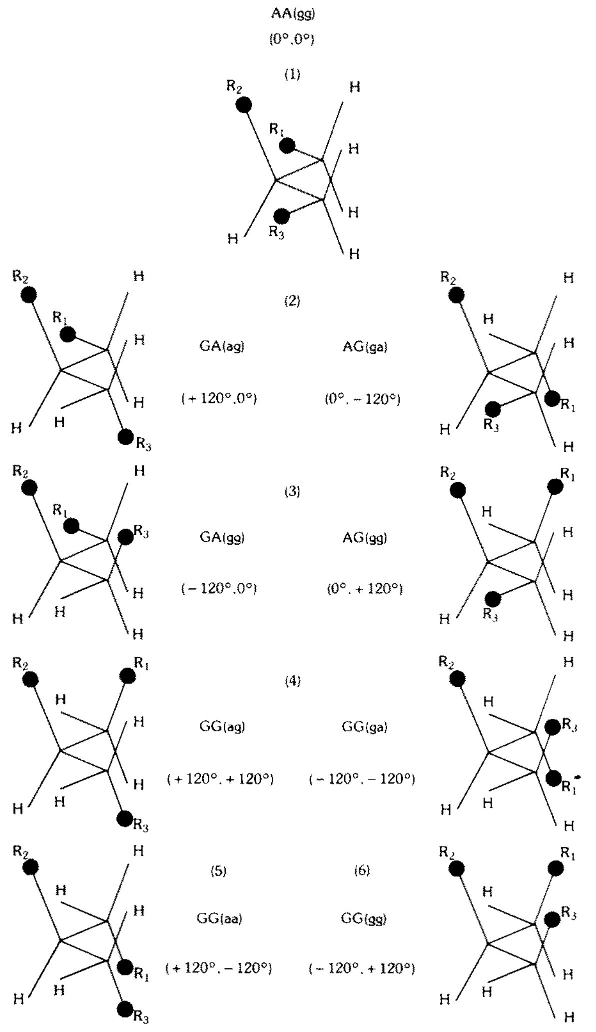


**FIG. 3. Possible conformations of the triglyceride structure.**

Chemical changes which then take place in the proposed reaction sequence are:

(i) $R_1$ C18:3(a) Conjugation of Δ15 (Fig. 4); (b) Hydrogenation of Δ14 (Fig. 5).

(ii) $R_1$ thus transformed is now identical to $R_2$. Either fatty chain may be attracted to the catalytic surface.

$R_1$ C18:2(a) Conjugation of Δ12 (*cis*) (Fig. 6); (b) Isomerization of Δ12 (*cis*)→Δ11 (*trans*) (Fig. 6); (c) Hydrogenation of Δ11 and isomerization of Δ9 (Fig. 7).

(iii) We can treat $R_2$ containing Δ9 (*cis*) and Δ12 (*cis*) in a slightly different manner by assuming initial participation of Δ9 (*cis*).

$R_2$ C18:2(a) Conjugation of Δ9 (*cis*) (Fig. 8); (b) Isomerization of Δ10 (*cis*)→Δ10 (*trans*) (Fig. 8); (c) Hydrogenation of Δ12 (*cis*) (Fig. 9).

(iv) The triglyceride now contains two fatty acid chains each having a *trans*-form ($R_1$ and $R_2$) and $R_3$ in our nomenclature has a *cis* form. Consequently, we see the following hydrogenation sequence to form the final tristearate.

(a) $R_3$C18:1 hydrogenation of Δ9 (*cis*) (Fig. 10).
(b) $R_1$C18:1 hydrogenation of Δ9 (*trans*) (Fig. 11).
(c) $R_2$C18:1 hydrogenation of Δ10 (*trans*) (Fig. 12).

As the subject reaction sequence proceeds, the spherical appearance of the original triglyceride develops into an arrangement similar to that of a tuning fork. A dimensional

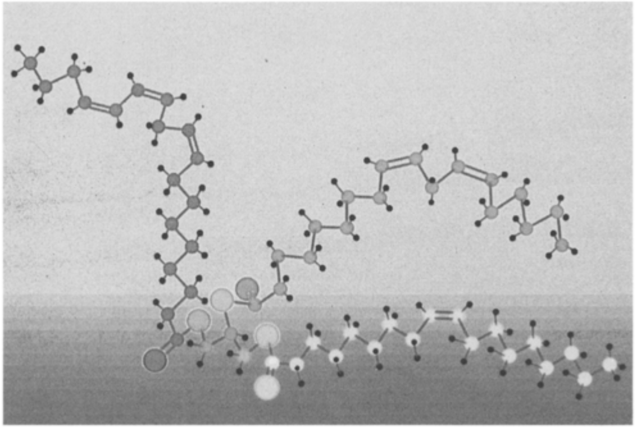


**FIG. 4. Conjugation of C18:3 prior to hydrogenation.**

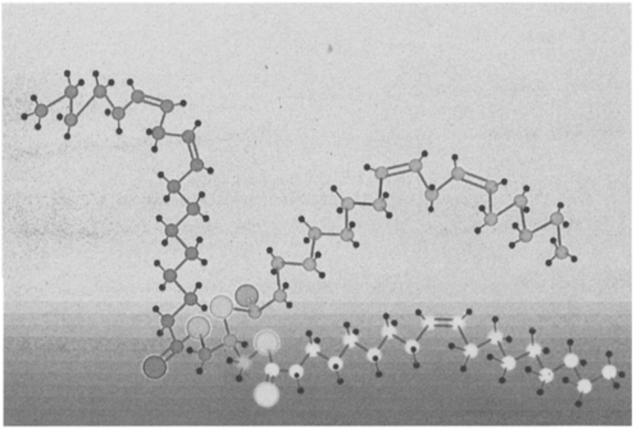


**FIG. 5. Hydrogenation of C18:3.**

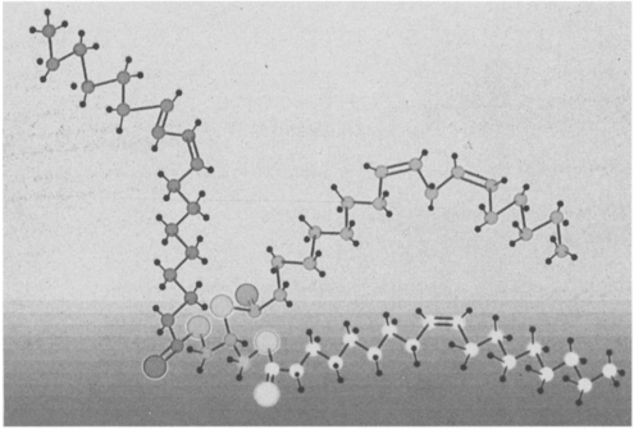


**FIG. 6. Conjugation of C18:2.**

alteration also accompanies the stereochemical changes. Calculations derived from computer study of the crystallography show that the starting triglyceride (Fig. 2) has a diameter of 1.4 nm, whereas the final tristearate is ca. 1.5 nm (Fig. 12).

A commercial operator who wishes to produce margarine and shortening feedstocks aims for a mixture of the compounds shown in Figures 5-8. When he wants a salad oil product, he will try to obtain as much as possible of the compound shown in Figure 5 (4).

Having established the problems involved on a molecular scale, one must try to achieve these changes by practical means.

## COMMERCIAL EQUIPMENT

So far, events have been shown taking place on a scale of 2 nm, whereas actual processing occurs in various commercial autoclaves with a diameter up to 1.5 m (5).

During the last several years, much attention has been drawn to heat preservation and many firms have installed devices to utilize or prevent loss of the thermal energy which is evolved as hydrogenation occurs. The hydrogenation itself is exothermic and a fall of one iodine value (IV) unit is sufficient to raise temperature in the autoclave by 1.6-1.7 C. This heat is extremely valuable and companies such as Buss A.G. of Switzerland have developed systems whereby the heat generated during hydrogenation is used to raise the temperature of the incoming oil by means of a heat exchanger (Fig. 13). (6).

By using this system one can save ca. 160 kg of steam and 2.5 $m^3$ of cooling water/ton of hydrogenated product. On a production unit of 100 ton/day of hydrogenated oil, the energy saving per year is 4,800 tons steam and 75,000 $m^3$ cooling water. In addition, the heat exchanger can produce a further 2,000 ton of steam at low pressure.

De Smet Belgium has also a dual autoclave system, incorporating a heat recovery installation (Fig. 14). The daily capacity of this plant is 100 ton/day and each autoclave has an oil charge of 7.5 tons. All operations are fully automated by means of a computer (private communication with A. Athanassiadis).

The tendency towards installation of heat-exchange equipment has gone side-by-side with improvements in process control. Systems offering precise gas-metering control and adjustable stirring speed are available from companies such as Franz Kirchfeld of Germany.

A drop in iodine value of one unit/ton of oil consumes 1.2 $Nm^3$ of hydrogen. The installation of a gas-metering system allows one to hydrogenate automatically to a given iodine value under standard conditions in the presence of a dependable catalyst. By variation of the stirring speed, the system operator has the ability to influence the steepness of the dilatometric curve of the product.

Thus, recognizing the importance of selectivity, let us consider the experimental measures to obtain selective reactions. By correlating the selectivity, the concentration of dissolved hydrogen, and its availability at the catalytic surface, Coenen summarizes the measures necessary to achieve maximum selectivity (Table III) (7).

However, the nature of the catalyst affects the selectivity most dramatically. A nonselective catalyst, even under optimally selective conditions will still produce a nonselective reaction. We therefore now try to answer the question

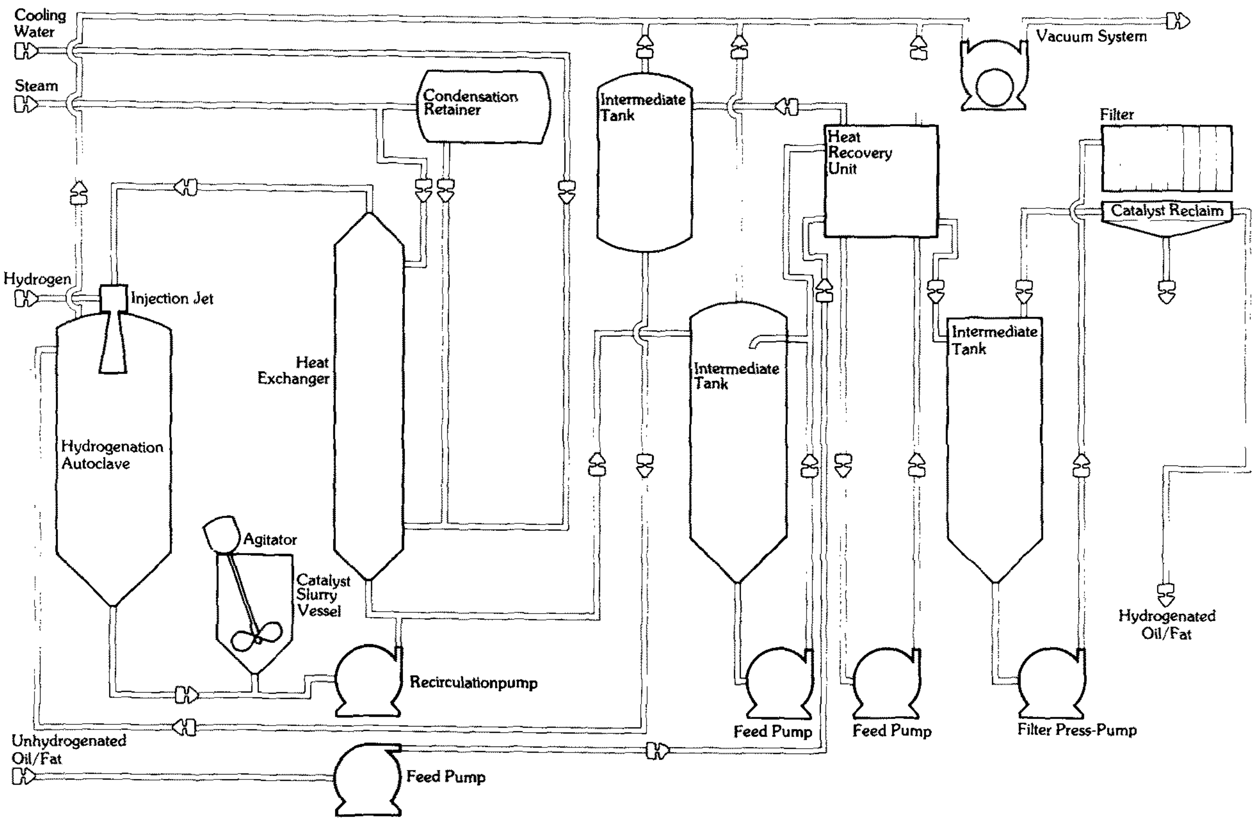


**FIG. 13. Buss reactor with heat recovery system.**

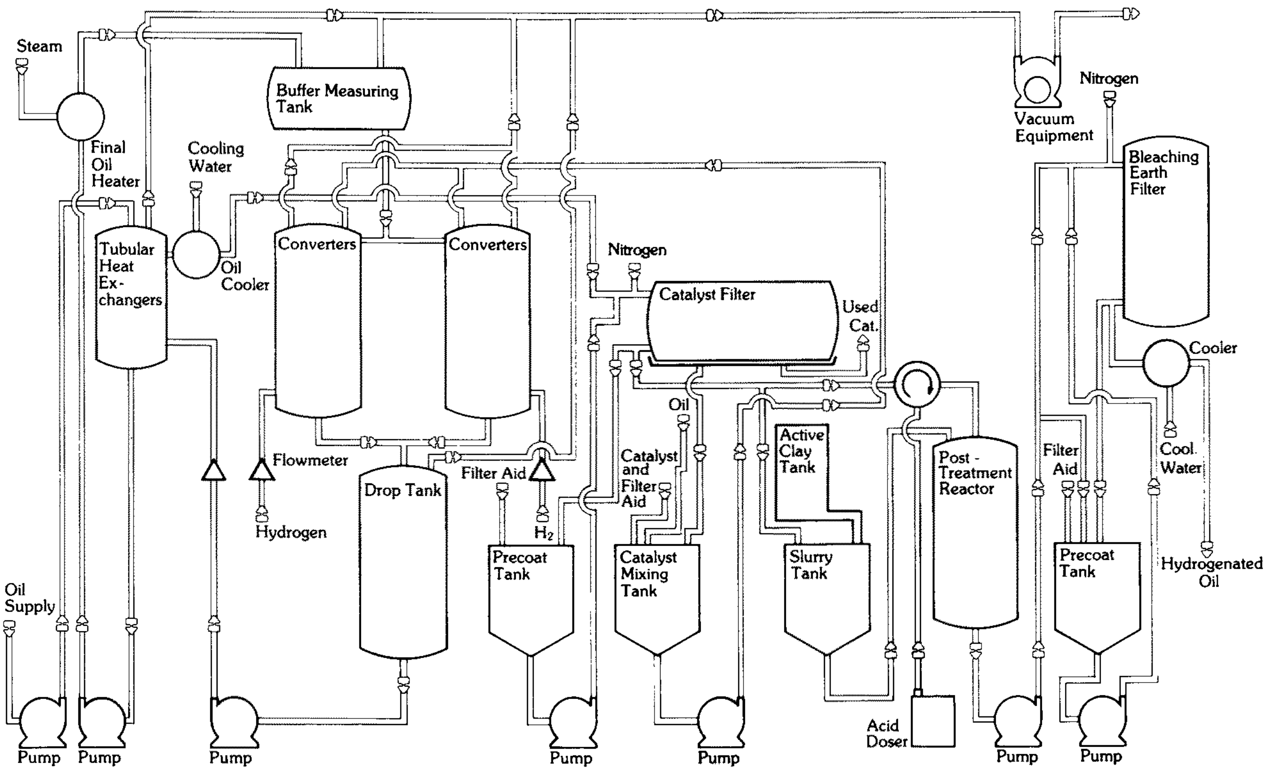


FIG. 14. De Smet hydrogenation system with heat recovery.

**TABLE III**

**Influence of Process Conditions on Dissolved Hydrogen Concentration near Catalyst Surface and on Selectivities $S_1$ and $S_I$**

| | Increase of | Effect on: $H_2$ concentration | $S_1$ | $S_{Isomerization}$ |
|---|---|---|---|---|
| Larger supply of hydrogen | Pressure | + | – | – |
| | Stirring intensity | + | – | – |
| | Temperature | – | + | + |
| Larger demand for hydrogen | Amount of catalyst | – | + | + |
| | Catalyst activity | – | + | + |
| | Degree of unsaturation in oil | – | + | + |

of what are the essential factors governing selectivity and preparation of a catalyst for that purpose.

## CATALYST PARAMETERS

A catalyst producer is faced with several contradictions when formulating his product and requires a compromise. The catalyst must exhibit both a high activity and a selectivity, while it is also essential that the catalyst can be filtered off very rapidly. The two objectives are incompatible. A very selective catalyst should have wide, shallow pores, which implies small particles. However, small particles lead to difficulties in filtration (Figs. 15 and 16) .

For a high activity and therefore a high poison resistance, small particles are also advantageous. (1 particle of 50 µm has the same volume as 4630 particles of 3 µm, and these particles have 17 times more geometric surface area as the 50 µm particle).

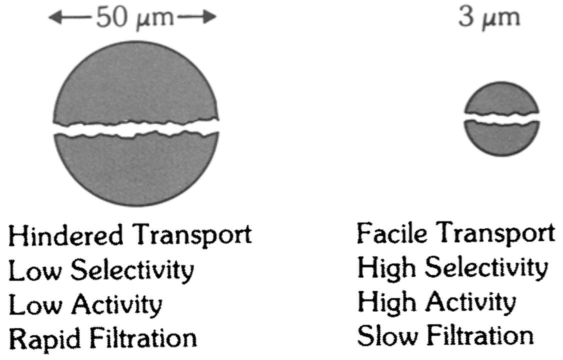


FIG. 15. Effect of relative catalyst particle sizes.

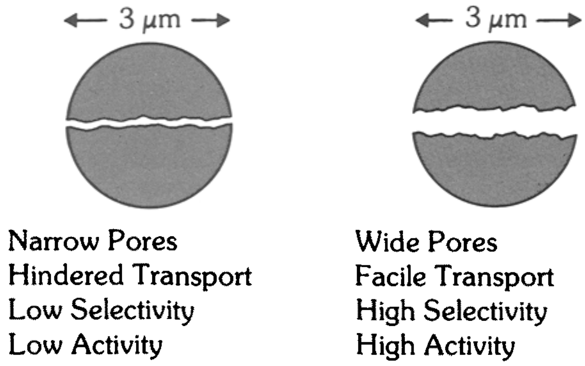


**FIG. 16. Effect of pore size on activity and selectivity.**

In order to facilitate the transport of the triglycerides through the pores, the pore dimensions should be of the order of at least 10 nm.

Preparation of such a structure in a porous solid requires the manufacturer to exert extremely tight controls during production. In principle, the ideal structure can be prepared.

Figure 17 is a series of photos to show the structure of a supported catalyst. In Figure 17(1), the structure of the diatomeous earth-support can clearly be seen. In photo (3), one can observe the macropore structure of the catalyst. Photo (4) shows the individual pores of this catalyst. The pores are between 20 nm and 70 nm. A pore wall is shown in photo (5). The black dots on this photo are the nickel crystallites, with an average diameter of 4 nm.

The overriding factor in determining the selectivity is the residence time of the triglycerides in the catalyst pore system. It predominates over the effect of process conditions as earlier described. The longer the residence time at the catalyst surface the greater is the probability of the occurrance of conjugation, isomerization, and hydrogenation.

## EFFECT OF SULPHUR

If it could be supposed that we now have the ideal catalyst, then one would assume that the task of preparing hydrogenated products becomes somewhat straightforward. Nature, however, provides a further complication in that raw materials contain impurities which modify the catalyst during hydrogenation, i.e., poisons.

Ivar Ottesen (8) studied the effect of various known hydrogenation catalyst poisons on activity. He utilized model compounds to effect the poisoning and arrived at the following conclusions: 1 ppm sulphur poisons 0.004% of nickel; 1 ppm phosphorus poisons 0.0008% of nickel; 1 ppm bromine poisons 0.00125% of nickel; and 1 ppm nitrogen poisons 0.0014% of nickel.

Because of the interaction between hydrogen and sulphur containing compounds at the catalyst surface, sulphur is released and becomes available for chemical reaction with nickel at the surface (9).

Reaction with sulphur inhibits the capacity of nickel to adsorb and dissociate hydrogen, reducing the total activity of the catalyst. As the ability of the nickel to hydrogenate is reduced, its tendency to promote isomerization is enhanced.

When hydrogenating rapeseed containing only 4.5 ppm sulphur, it can be clearly demonstrated that sulphur contamination has this effect (10). The oil is hydrogenated using two catalyst concentrations; 0.02% as nickel and 0.05% as nickel (Fig. 18).

The hydrogenations are done under identical conditions and using Coenen's criteria, we should expect that using a catalyst level of 0.02% nickel, the surface concentration of hydrogen will be greater, thus the likelihood of *trans*-isomer formation will be less. We observe that this is not the case in practice and higher *trans*-isomer levels are seen at the lower nickel concentration. The reason is that since the nickel level of 0.02% is lower, the nickel surface available to adsorb sulphur is also smaller and consequently the number of catalytic sites which can adsorb and dissociate hydrogen is necessarily reduced as poisoning takes place. Thus, the triglycerides have a very high logistic chance of being adsorbed on a sulphur poisoned site, which they have no choice but to leave in the *trans*-isomer form.

This phenomenon has been used by catalyst manufacturers and oil processors alike to obtain a product with a very high *trans*-isomer content. The main attraction is a relatively high melting point at high iodine value, and thus a very steep dilatometric curve, which is required, e.g., for hard base stocks or cocoa-butter extenders/substitutes (Fig. 19) (11).

It is interesting to note that commercially produced catalysts which are previously sulphur treated have a much more consistent and selective performance with respect to selectivity than catalysts which are purposely sulphur poisoned in situ by fats and oils processors.

## FORMATION OF AROMATICS

An important factor associated with the surface adsorption of sulphur is the formation of aromatic byproducts. Ong found that at temperatures above 180 C, highly unsaturated triglycerides in the presence of palladium and nickel-sulphur catalysts, aromatics can be formed (12). Marine-based oils, which are highly unsaturated, also contain relatively high amounts of sulphur.

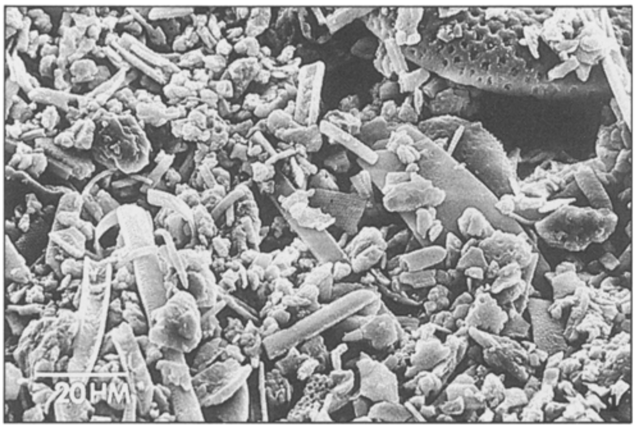
Urdahl, Sääv and Helegrud found that the sulphur present in marine oils is generated by post-mortal reactions in fish (13).

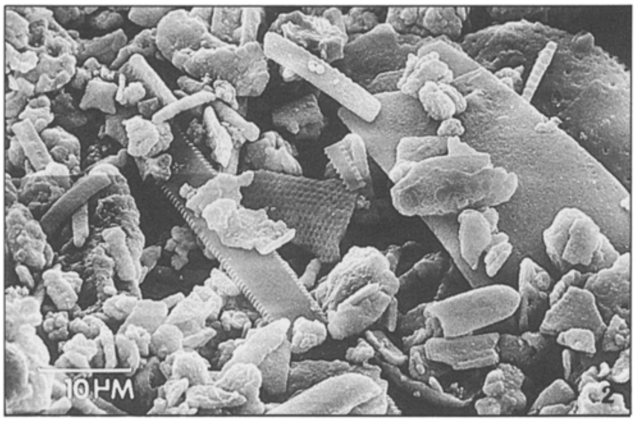
The amount of sulphur which is dissolved in "pressed out" marine oils is proportional to the storage time of the fish before processing. As catches dwindle and fishing boats spend consequently more time at sea, then the rise in sulphur levels in marine oils over the last years can be explained.

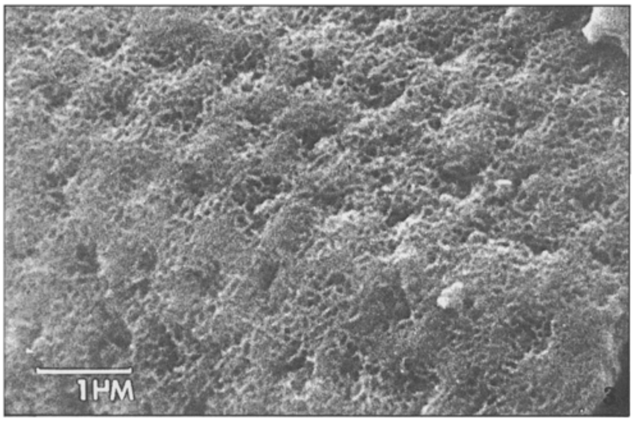
Ong suggests a two-step hydrogenation process in order to keep aromatic formation below the detection limit (Fig. 20). When hydrogen availability is low, sulphur-poisoned nickel surfaces promote conjugation, cyclization and dehydrogenation (Fig. 21). When the iodine value of the oil being hydrogenated is below 120, hardly any triunsaturated systems are present, and at that point the pressure can be reduced for selectivity reasons. In older hydrogenation systems, hydrogen cannot be transported as fast as it is consumed during the initial stages of the hardening process. In systems where only low hydrogen pressures in the early stages of the process are possible, the hydrogen transport should be improved.

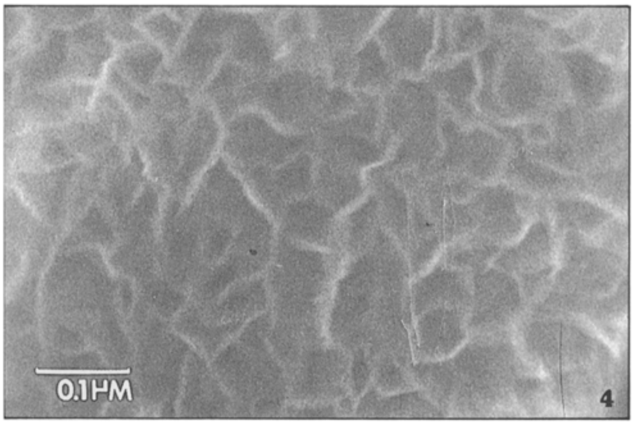
## EFFECT OF PHOSPHORUS

Whereas sulphur primarily affects the activity of a hydrogenation catalyst, the presence of phosphorus in the form of phosphatides mainly affects selectivity. During physical refining of soybean oil, the phosphorus content may become as high as 10 ppm. Even in the conventional processes of caustic washing and treatment with bleaching earth, phosphatides may still be present in the pretreated oil. As









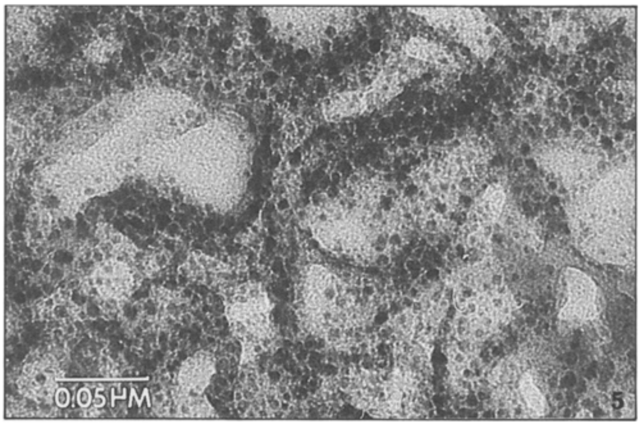


**FIG. 17. Structure of a catalyst. (1) An ideal catalyst; (2) part of photo 1; (3) part of photo 2; (4) individual pores of the catalyst; (5) pore wall.**

shown earlier, the poisoning effect of phosphorus in lecithin and phosphatides is somewhat less than that of sulphur. Ottessen also showed the influence of phosphatides on selectivity when hydrogenating soybean oil (Table IV) (14).

He asserts that the cause of this occurrence is that the phosphatides tend to reside at the pore entrances and hinder the exit of the triglycerides already in the pore. This should be more marked in catalysts having small pores. The result is a higher degree of saturation in the triglycerides. Moreover, due to a high hydrogen concentration at the nickel surface compared to the relatively low availability of double bonds to be hydrogenated, the *trans*-isomer content in the product will decrease with increasing phosphatide content (Table V).

## COLOR INTERFERENCE

Hydrogenation must lead to products of well defined melting behavior (dilatation) and taste. The physical color of the product is also of consumer importance.

Fish and vegetable oils which are not properly alkali-refined and bleached can still contain the hydrolysis products of the chlorophyll type, e.g., pheophytins which can cause green coloration. The presence of these green pigments is masked in unhydrogenated, crude or prerefined oils by yellow pigments which are often of the carotenoid type.

Both temperature increase and double bond hydrogenation remove the color contribution of the carotenoids.

Green coloration attributable to impurities of the chlorophyll type can be present in both seed-based and marine-based oils as fish also feed on algae.

The color interference occasioned by the pheophytin derivatives can be removed by a postbleaching step following hydrogenation. Pheophytin is the form of chlorophyll which is not coordinated with magnesium (15).

Nitrogen atoms in the porphyrin ring of pheophytin are attached to hydrogen atoms. If free fatty acids have formed nickel soaps in an oil where free pheophytin is present, the nickel may also participate in the formation of a coordinated complex.

The principal cause of chlorophyll in soybean and rapeseed is freezing before the seed has been sufficiently matured. A proportion of the chlorophyll will remain in the oil when extracted and is very difficult to remove with conventional bleaching earth.

ACKNOWLEDGMENT

The author is grateful for the assistance of B. Beagley, P.M. Gilbert and H.P. Heltzel in the preparation of this paper.

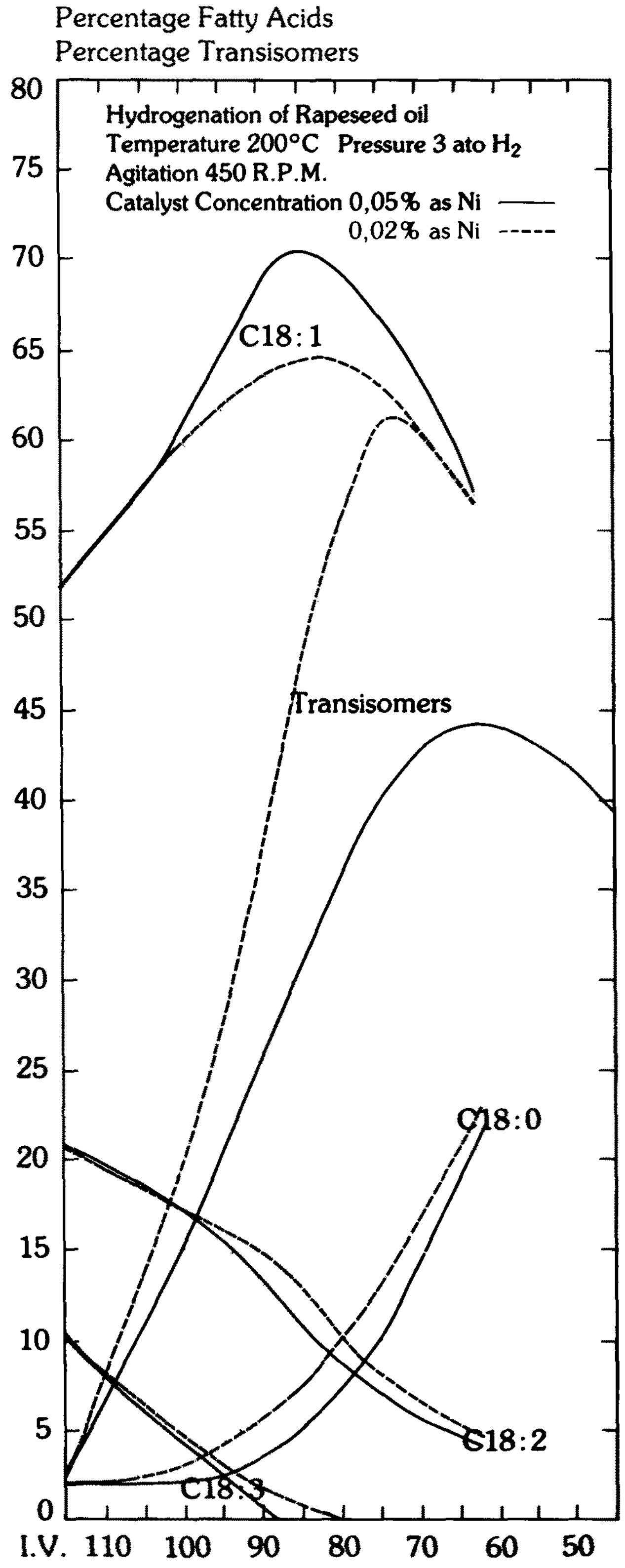


FIG. 18. Influence of catalyst concentration at constant temperature and pressure.

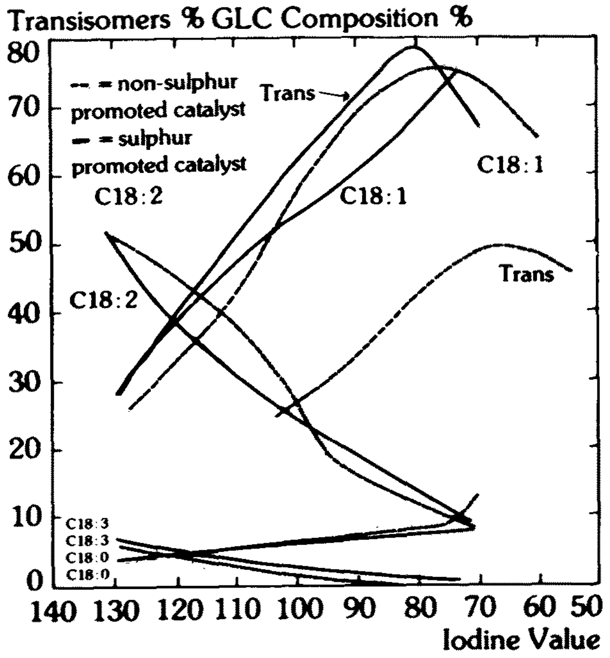


FIG. 19. Comparison of GLC composition and *trans*-isomer content, when partially hydrogenating soybean oil with a sulfur- and a non-sulfur-promoted catalyst.

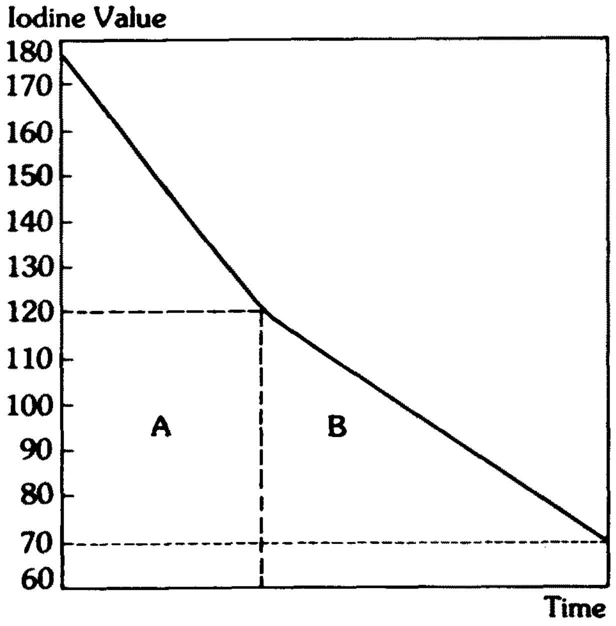


FIG. 20. Two-phase hydrogenation of highly unsaturated oils in order to avoid aromatic formation. Reaction conditions: (A) 200 C; 4 bar $H_2$; up to an iodine value of 120. (B) 200 C; 1 bar $H_2$; up to an iodine value of, e.g., 70. Nickel content: function of S-content in the oil.

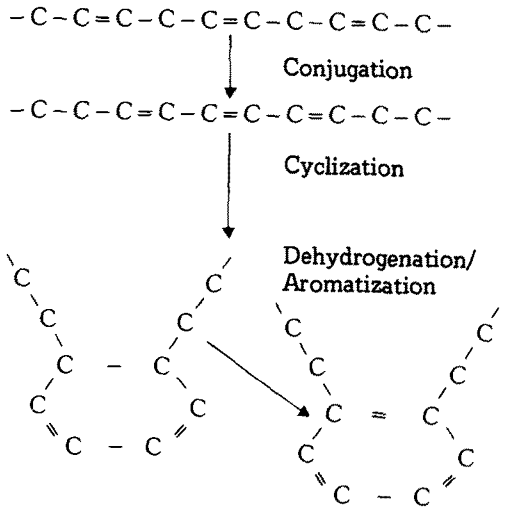


FIG. 21. Formation of aromatic compounds out of triunsaturated fatty acid systems.

## REFERENCES

1. Haraldsson, G., Proceedings of the Symposium on Hydrogenation of Oils, Rimini, 1980.
2. Frankel, E.N., in Handbook of Soy Oil Processing and Utilisation, American Soybean Association, St. Louis, MO, and the American Oil Chemists' Society, Champaign, IL, 1980, chap. 14.
3. Stølevik, R., Chem. Scand. A 28 3 (1974).
4. Partial Hydrogenation of Soya-bean Oil with Nysel DM-3 and its Consequent Winterisation, Harshaw Chemie B.V., De Meern, Holland.
5. Hastert, R., JAOCS 58:169 (1981).
6. Duveen, R., and G. Leuteritz, Fette, Seifen, Anstrichm. 1 Sonderheft (1982).
7. Coenen, J., Proceedings of the Symposium on Hydrogenation of Oils, Rimini, 1980.
8. Ottessen, I., Presentation at the 6th Scandinavian Symposium of Fats and Oils, Grena, Denmark, 1971.
9. Klostermann, K., and H. Hobert, J. Catal. 63:355 (1980).
10. Nysel DM-3 brochure, Test results on Rapeseed Oil, Harshaw Chemie B.V., De Meern, Holland.
11. Harshaw Catalysts, Technical Bulletin no. 902, Nysel SP-7, The Harshaw Chemiçal Co., Beachwood, OH.
12. Ong, T., Fette Seifen, Anstrichm. 12 (1969).
13. Urdahl, H., H. Sääv and A. Helegrud, Paper presented at the 11th World Congress of ISF, Gøteborg, Sweden, 1972.
14. Ottessen, I., and B. Jensen, Paper presented at the ISF/AOCS Congress, New York, 1980.
15. Nielsen, R., Derivatives of Pheophytin in Hydrogenated Fish Oil, Nordiske Fedtsymposium Porøs.

**TABLE IV**

**Effect of Phosphorus on Selectivity when Hydrogenating Soybean Oil**

| Added Lecithin[a] | C18:0 | C18:1 | C18:2 | C18:3 | Iodine Value |
|---|---|---|---|---|---|
| 0 ppm phosphorus | 15.7 | 69.8 | 3.6 | 0 | 67.3 |
| 4 ppm phosphorus | 18.0 | 65.2 | 5.9 | 0 | 67.1 |
| 8 ppm phosphorus | 33.0 | 41.8 | 13.8 | 0.5 | 66.1 |

[a] Lecithin = Stearyl - Palmitoyl - Choline.

**TABLE V**

**Effect of Phosphorus on *trans*-Isomer Formation, NMR Values and Slip Melting Point (at an IV of approximately 67)**

| Added lecithin | Slip MP (C) | NMR 20 | NMR 30 | % *trans*-Isomers |
|---|---|---|---|---|
| 0 ppm phosphorus | 42,5 | 63 | 32 | 49 |
| 4 ppm phosphorus | 47,5 | 54 | 30 | 41 |
| 8 ppm phosphorus | 59,0 | 54 | 43 | 24 |