TABLE IV

TLC Separation of Reaction Mixture of Triolein Synthesis with *C. rugosa* Lipase after 1 hr Reaction Time at 25 C

Component	wt %
2-Monoglyceride	0.37
1-Monoglyceride	2.26
1,2-Diglyceride	0.86
1,3-Diglyceride	3.48
Triglyceride	1.76
Fatty acid	91.26

bial spoilage was essentially eliminated because of low temperature. Stock solutions thus prepared remained stable for several months without loss of enzyme activity.

To drive the reaction towards esterification, we used a 50% excess of fatty acid and reduced water activity by distilling out water periodically at room temperature with the aid of a vacuum pump. Some problems may occur with this technique. If too much water was pumped off, the enzyme precipitated, stopping catalytic activity. However, addition of a small amount of water redissolved the precipitate and restored enzyme activity. It was found that the emulsion, formed after a few hours of reaction, contains large droplets and required homogenization to form droplets of ca. 3 microns. This usually prevented precipitation.

Enzymatic esterification was readily followed by analysis of free fatty acid contents and by IR spectrophotometry, which showed a gradually growing ester peak at 1740 cm^{-1} and a correspondingly shrinking acid peak at 1710 cm^{-1}. TLC separation showed that all expected mono-, di-, and triglycerides were formed after a 1-hr reaction time as shown in Table IV, and it should be noted that triglyceride was present even at this early stage of esterification. As mentioned above, the reaction slowed down and after a 6-week reaction time esterification of all hydroxyl groups was ca. 80% complete. We were not able to make the reaction proceed further, presumably because equilibrium had been attained. A TLC analysis of a 6-week reaction product showed 1.4% monoglycerides, 19.8% diglycerides, 43.6% triglycerides and 35.3% fatty acids. The same esterification of glycerol and oleic acid could also be run with the lipase from *A. niger*, and the results obtained were essentially the same as those with the *C. rugosa* lipase. The enzymes were still highly active after 6 weeks and hydrolyzed the glyceride mixture overnight in the presence of water.

Fatty acids can be esterified with various alcohols other than glycerol (7). We also found that sorbitol would not esterify oleic acid. Ethylene glycol and diethylene glycol esterify slowly and incompletely. Benzyl alcohol esterified to 90-95% in ca. 6 weeks. We were not able to esterify methanol and oleic acid with *C. rugosa* lipase. Because of the slowness of these esterifications, as developed up to the present, this information is of scientific rather than practical industrial interest. However, conceivably more active and less costly enzymes may become available and a superior process for enzymatic esterification may be developed in the future.

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Partial Hydrogenation of Polyunsaturated Fatty Materials

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ABSTRACT

For many applications involving the use of polyunsaturated triglycerides such as soybean oil, a liquid product having an improved stability to oxidation is required. The partial hydrogenation of soybean oil into a liquid product containing less oxidizable materials can be achieved with selective nickel catalysts. A soybean oil containing ca. 5% solid matter at 10 C, 1% linolenic acid and 0.5% conjugated dienes is obtained with a nickel/titanium oxide catalyst or with nickel-zirconium oxide/kieselguhr catalyst treated with fatty amines such as lauric or coco primary amines. In the frame of this work, ca. 100 heterogeneous Ni catalysts have been tested under standard operating conditions for the partial hydrogenation of soybean oil.

INTRODUCTION

This paper concerns a process for selective hydrogenation of natural oils or possibly fatty acids to reduce their content of polyunsaturated compounds while limiting the formation of solid compounds. Some vegetable oils, such as soybean oil, linseed oil or rapeseed oil, contain trienic and dienic compounds in admixture with monoenic and saturated compounds. To use these oils as edible oils or to prepare fatty acids for paints and industrial applications, it is often advantageous to increase their stability. During the partial hydrogenation, it is then of prime importance to limit: (a) the formation of saturated compounds: polyenic compounds must therefore be hydrogenated to dienic and monoenic compounds; (b) the isomerization of *cis* to *trans* isomers: however, isomerization always occurs during hydrogenation and this isomerization results in the formation of solid products; and (c) the formation of conjugated compounds which are unstable.

To fulfill these requirements, a highly selective catalyst is needed. Homogeneous (1-3) or heterogeneous catalysts based on copper (4-6), copper-chromite (7), palladium (8) or nickel (9-18) are often mentioned in the literature. About 100 nickel catalysts have been prepared or modified and tested under standard operating conditions for this work. Two patents have been granted (17,18).

THEORETICAL ASPECT

Selectivity Concept

For the partial hydrogenation of polyunsaturated triglycerides, three different types of selectivity are usually defined (Table I):

TABLE I

Selectivity Definitions

Reactions

$$C18{:}3 \xrightarrow[k_3]{} C18{:}2 \xrightarrow[k_2]{} C18{:}1 \xrightarrow[k_1]{} C18{:}0$$

Selectivity

Linolenic selectivity (S_{II} or SL_n)	$S_{II} = k_3/k_2$
Linoleic selectivity (S_I or SL_o)	$S_I = k_2/k_1$
Specific isomerization (S_i)	$S_i = \dfrac{\text{number of } \textit{trans} \text{ double bonds formed}}{\text{number of hydrogenated double bonds}}$

—the linolenic selectivity S_{II} or SL_n defined as being the rate constants ratio k_3/k_2,

—the linoleic selectivity S_I or SL_o defined as being the rate constants ratio k_2/k_1,

—the specific isomerization S_i defined as being the ratio of number of *trans* double bonds formed/number or hydrogenated double bonds.

A high S_{II} means that high yields of dienoic are obtained. A high S_I means that high yields of monoene are obtained. A high S_i means that sizeable *cis* to *trans* isomerization occurs. The main factors governing selectivity of the reaction are operating conditions and nature of the catalyst.

Operating Conditions

The approach of the reactants to the catalyst surface and the concentration of these reactants (oil and hydrogen) at the catalyst surface are data-related to the reaction selectivity and depend on the operating conditions. The influence of the operating conditions on the reaction selectivity has been well studied by Coenen (15) (Table II).

It has been observed when hydrogenating with Ni catalysts that increases of pressure and stirring intensity, conditions that raise the hydrogen concentration near the catalyst surface, result in a decrease in linoleate selectivity S_I and S_i of the reaction. Conditions that lower the hydrogen concentration near the catalyst surface, such as temperature, catalyst concentration, catalyst activity and the oil unsaturation level, at the same time increase S_I and S_i.

The Horiuti-Polanyi theory explains these observations rather well (Table III). Contacting Ni metal with hydrogen and unsaturated molecules, we will find hydrogen atoms and unsaturated molecules bonded to the nickel in an activated state. The hydrogenation goes through a half-hydrogenated step, which can follow four different pathways:

TABLE II

Influence of Process Conditions on Dissolved Hydrogen Concentration near Catalyst and on Selectivities S_I and S_i (15)

Increase of		Effect on		
		(H_2)	S_I	S_i
Increase supply	pressure	+	−	−
	stirring intensity	+	−	−
Increase demand	temperature	−	+	+
	catalyst amount	−	+	+
	catalyst activity	−	+	+
	unsaturation of oil	−	+	+

(a) The half-hydrogenated state takes a second hydrogen from the surface. The desorption results in the completely hydrogenated molecule.

(b) The hydrogen H_a returns to the nickel surface and the original molecule is desorbed.

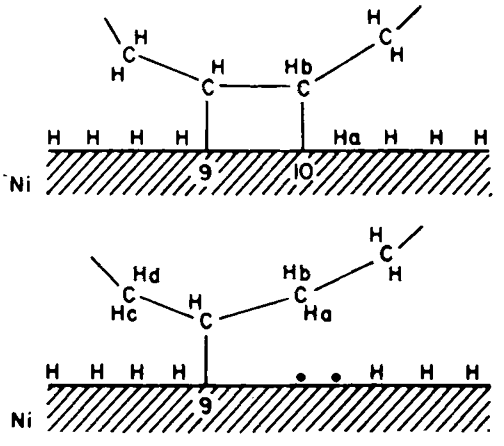
(c) The hydrogen H_b returns to the nickel surface and *cis-trans* isomerization is observed in the desorbed molecule.

(d) The hydrogen H_c or H_d returns to the nickel surface and a shift of the double bond is observed in the desorbed molecule.

A high concentration of dissolved hydrogen or a high

TABLE III

Horiuti-Polanyi Mechanism for the Hydrogenation of Unsaturated or Polyunsaturated Fatty Acids



H_2 and unsaturated molecule bonded to the nickel surface

Half-hydrogenated state

coverage of the catalyst surface with hydrogen results in rapid hydrogenation of double bonds and low selectivity. With low hydrogen coverage, the isomerization mechanisms will be favored over the completion of the hydrogenation. Coenen postulated that either monoenic or polyenic acids are initially bonded with one double bond. With low hydrogen coverage, adsorbed linolenic or linoleic acid may split off a hydrogen atom from its reactive methylene group and become bonded to the catalyst surface with three carbon atoms. It has been proposed that this permits bondings of a second double bond to the catalyst surface and increases the bonding strength of linolenic or linoleic acid over that of oleic acid: there is monopolization of the catalyst surface by the polyenic acids and large reactivity differences therefore result. Relative reactivities of oleic, linoleic and linolenic acids are 1, 20 and 40, respectively.

Catalyst

Copper, copper-chromite, palladium and nickel are the most common metals used as active species in heterogeneous catalysts for partial hydrogenation of polyunsaturated triglycerides. However, hydrogenation with nickel catalysts has been the choice of industry, largely due to the availability, low cost and inert nature of the metal to the oil. Our hydrogenation tests are also made in presence of nickel-based catalysts.

Since the catalytic reaction takes place on the surface of the Ni metal, an active nickel catalyst will need a large specific nickel surface area. This can only be achieved by bringing the metal into an extreme subdivision. A practically used catalyst generally contains nickel crystallites of a size of only 40-50 Å. To maintain the nickel in its subdivided state to prevent sintering and at the same time to facilitate filtration of the catalyst from the oil after hydrogenation, the nickel crystallites are attached to a porous support (kieselguhr-silica-alumina, mostly) of a particle size of the order of 10^4-10^5 Å. Most of the nickel area is hidden in the narrow channels of the porous catalyst particles. Coenen et al. (15) distinguish three pore sizes:

- –those with a diameter less than 20Å which are inactive with regard to fat hydrogenation since triglycerides cannot diffuse into them; the large triglyceride molecules have a diameter (if considered as spheres) of 15 Å;
- –those with a diameter of 100Å or more, which allow easy diffusion and for which there is a good correlation between catalyst activity and surface area; in such instances, selectivity can be correlated with the ratio of the number of wide pores to intermediate pores;
- –those with a diameter in between which only allow a restricted diffusion.

In general, we can say that the pore diameter is between 200 and 700Å. The selectivity is largely dependent on the residence time in the catalyst pores. A long residence time means more possibilities of conjugation, isomerization and hydrogenation.

Naturally, the intrinsic character of the support (kieselguhr-silica-alumina) – especially its acid character – is also a factor to consider. Even on powdered glass surfaces, both Lewis-type acid sites and Brönsted acid sites have been demonstrated. The acid sites – especially the Brönsted acid sites – are known to favor the isomerization reactions.

According to Achaya et al. (21), the presence of potassium soaps appears to poison acidic sites leading to less hydrogen dissociation and to suppression of the *cis-trans* monoene isomerization. When preparing catalysts, the acidic sites are also suppressed when nickel is precipitated from its salts with strong alkali solutions: the catalyst is then active for hydrogenation reactions (22).

An acidic material, when present, enhances hydrogen dissociation and greatly speeds up the hydrogenation reaction without affecting the desorption-isomerization reactions.

When preparing our nickel catalysts and when selecting our standard operating conditions, we have taken these theoretical data into account: we have mainly modified the nature and the acidity of the carriers.

OPERATING PROCEDURE

The same soybean oil feed was used for all the described tests (Table IV). The tests were done in a 20-L stainless steel reactor: 10 L soybean oil was loaded for a hydrogenation test. The stirring was performed by a 4 m^3/hr hydrogen stream (STP): the tests was made at 140 C under a 3 kg/cm^2 pressure and with a 0.1% Ni concentration.

The hydrogenation reaction was followed with refractive index of the product. The reaction was stopped at an iodine value of 100: when reached, this corresponds to a refractive index of $15^\circ 50'$ at 50 C.

In this paper, the term "activity" is defined as being the time, in min, needed to reach an iodine value of 100 under the standard operating conditions.

Analytical Procedures

The following analytical procedures were used to characterize the final hydrogenated product.

Vapor phase chromatography (VPC) (on methyl esters). At 190 C (isothermal) on a 2.2 m column (1.75 m polyethyleneglycol adipate and 0.45 m carbowax).

% trans (on methyl esters). Infrared (IR) spectrometry by comparing the intensity of the bands at 10.3 u corresponding to a known concentration of methyl elaidate and to the sample.

Iodine value. I.P. 84.

Nuclear magnetic resonance (NMR) curve. NMR low resolution apparatus is used to determine the percentage solid at different temperatures (19).

Conjugated dienes. AOCS Method Ti-la-64.

RESULTS

Four different catalyst types were prepared or modified and tested for soybean oil hydrogenation: (a) nickel and promoted nickel catalysts on conventional carriers, e.g., kieselguhr; (b) nickel catalysts on various carriers; (c) nickel on kieselguhr catalysts treated with basic organic nitrogen-containing compounds; and (d) nickel on kieselguhr catalysts treated with traces of basic nitrogen-containing compounds added to the feed.

According to the literature (20), the less acid catalysts like those listed under (b), (c) and (d) would make the retention of the *cis* configuration of the natural products easier.

Nickel on Kieselguhr Catalysts

Two Ni on kieselguhr catalysts, one unpromoted (ref 24/8)

TABLE IV

Soybean Oil Feed Analysis

Iodine value: 135.8	VPC composition (%)
% Free fatty acids: 0.03	
Peroxide content: 0 meq/kg	C16:0:11.0
Phosphorus content: 0 ppm	C18:0:3.9
Color (Lovibond): 2Y-0.2R	C18:1:22.3
	C18:2:55.0
	C18:3:7.3

and the other promoted with zirconium oxide (ref 24/9) have been chosen as references (Table V).

TABLE V

Nickel on Kieselguhr Catalysts Used as References

	Ref 24/8	Ref 24/9
% Nickel	23.5	22.7
% Kieselguhr	12	11.8
% Protective fatty layer	64.5	64.1
% Promoter (ZrO_2)	–	1.4

A series of Ni on kieselguhr catalysts promoted with various metallic oxides (ZrO_2, TiO_2, Ce_2O_3, ThO_2, Bi_2O_3, GeO_2, MnO_2, Fe_2O_3, ZnO) or with different alkaline earth oxides (MgO, CaO) have been synthesized and tested. With most of the promoted catalysts, no large improvements were observed compared with the unpromoted ones. Only the catalyst promoted with cerium oxide gave very interesting results with only 4.9% solid material at 10 C, as shown in Table VI.

TABLE VI

Results Obtained with the Ce_2O_3 Promoted Ni/Kieselguhr Catalyst

	Unpromoted	Promoted with Ce_2O_3
Activity (min)	64	55
C18:0	9	6.5
C18:1	44.6	48.2
C18:2	32	31
C18:3	1.8	1.5
% *trans*	15.3	18.5
% Solid at 10 C	13.3	4.9

Nickel Catalysts on Various Carriers

Metal oxides (TiO_2, MoO_3, WO_3, ZnO) and alkaline earth oxides (MgO, CaO) were used as carriers instead of kieselguhr when preparing Ni catalysts. Only when TiO_2 was used as carrier, the soybean oil hydrogenation tests showed outstanding results: the most selective one among the prepared TiO_2 supported catalysts gave hardly 4.0% solid material at 10 C in the hydrogenated triglyceride, i.e., the lowest solid content reached with the catalysts tested in this study (Table VII). Furthermore, only 0.4% conjugated diene has been found in the final product.

TABLE VII

Results Obtained with the Most Selective Ni/TiO_2 Catalyst

	Ref 24/8 (Ni/kieselguhr)	Ni/TiO_2
Activity (min)	64	53.5
C18:0	9	6
C18:1	44.6	48.3
C18:2	32	30.8
C18:3	1.8	1
% *trans*	15.3	18.5
% Solid at 10 C	13.3	4

Nickel Catalyst Treated with Ammonia or Amines

The two Ni on kieselguhr reference catalysts ref 24/8 and ref 24/9 were treated with various nitrogen compounds including ammonia, urea and aliphatic amines containing one or four nitrogen atoms (diethylamine, triethylamine, tributylamine, *n*-butylamine, fatty amines, hexamethylene tetramine).

When the starting Ni catalyst was treated with an aliphatic amine, a low melting point amine was preferred to avoid the presence of heavy components in the reaction mixture. As a total result, a significant decrease of the content in solid matter at 10 C was observed with all these basic nitrogen compounds treated catalysts: this phenomenon is mainly due to a restricted formation of stearic acid from oleic acid as no real improvement of the retention of the *cis* configuration was observed. In addition, no large drop in catalyst activity occured. The best result was obtained with the Ni-ZrO_2/kieselguhr catalyst (ref 24/9) treated with a coco primary amine: only 4.8% solid matter at 10 C and 0.2% conjugated diene were found in the hydrogenated soybean oil (Table VIII).

TABLE VIII

Results Obtained with a Ni-ZrO_2/Kieselguhr Catalyst (Ref 24/9) treated with a Coco Primary Amine

	Ref 24/9	Ref 24/9 treated with coco primary amine[a]
Activity (min)	67.5	75
C18:0	8.1	5.7
C18:1	45.3	50
C18:2	31.5	30.5
C18:3	1.7	1
% *trans*	18.1	18
% Solid at 10 C	12.4	4.8

[a] N/100 Ni (at/at):9.8.

The amount of nitrogen fixed on the catalyst surface influences the selectivity but has no marked effect on the activity. A definite correlation between the ratio N/100 Ni (at/at) and the amount of solid material at 10 C or the stearic formation is observed with the Ni/kieselguhr catalyst (ref 24/8): the higher the N/100 Ni ratio the lower the percentage solid at 10 C and the stearic acid formation (Table IX).

TABLE IX

Influence of the N/100 Ni Ratio on Activity and Selectivity of an Amine-Treated Ni/Kieselguhr Catalyst (Ref 24/8)

N/100 Ni (at/at)[a]	Activity (min)	C18:0	% *trans*	% Solid at 10 C
0	64	9	15.3	13.3
10	62	7.8	14.5	9.1
20	64	6.8	14.5	6.3
30	63	6.7	16	4.9

[a] Catalyst ref 24/8 treated with coco primary amine.

The chemical nature of the nitrogen compound used is important. By treating the same Ni/kieselguhr catalyst (ref 24/8) with various nitrogen compounds to obtain an identical N/100 Ni ratio of 20, significant differences of the solid content into the hydrogenated soybean oil were observed, as shown in Table X: ammonia and primary amines lead to lower solid contents then tertiary amines.

Nickel Catalysts in Presence of a Feed Doped with Basic Nitrogen Compounds

Hydrogenation tests on soybean oil doped with various fatty amines have been run in the presence of Ni/kieselguhr catalysts ref 24/8 and ref 24/9. The catalyst ref 24/9 gave outstanding results with a soybean oil feed doped with lauric primary amine (Table XI): its activity is slightly

TABLE X

Results Obtained with a Ni/Kieselguhr Catalyst (Ref 24/8) Treated with Various Basic Nitrogen Compounds

Basic nitrogen compound	N/100Ni	Activity (min)	C18:0	C18:1	C18:2	C18:3	% *trans*	% Solid at 10 C
None	0	67.5	8.1	45.3	31.5	1.7	18.1	12.4
$(C_2H_5)_3N$	20	62	8.1	46.1	31.5	1.3	16	10.3
$(C_4H_9)_3N$	20	64	8	46.3	31.3	1.7	16.2	8.9
$(C_2H_5)_2NH$	20	60	7.7	46.5	31.7	1.7	15.4	7.5
$C_4H_9NH_2$	20	61	7	48	31	1.3	17.2	7.3
NH_3	20	64	7	48	31.5	1.1	15.8	5.1

TABLE XI

Results Obtained with the Ni-ZrO_2/Kieselguhr Catalyst (Ref 24/9) by Adding Lauric Primary Amine to the Feed (N/100 Ni=10)

	Ref 24/9	Ref 24/9 + lauryl amine
Activity (min)	67.5	77
C18:0	8.1	5.7
C18:1	45.3	49.8
C18:2	31.5	30
C18:3	1.7	1
% *trans*	18.1	17
% Solid at 10 C	12.4	4.2

decreased but its selectivity greatly improved as th hydrogenated soybean oil only contains 4.2% solid matter at 10 C and 0.1% dienes.

According to hydrogenation tests made in a 1-L Parr bomb in the presence of catalyst ref 24/9 at a temperature of 120 C instead of 140 C, the effects on the catalyst could be very dependent on the chemical structure of the fatty amines added to the feed: the primary fatty amines moderately reduce the activity and increase the selectivity as secondary and tertiary fatty amines markedly decrease both activity and selectivity of the catalyst.

Table XII compares the results obtained by both treatments with basic nitrogen chemicals, i.e., the introduction of nitrogen derivatives into the feed and the treatment of the catalyst itself before the hydrogenation test. A slight activity decrease but a significant selectivity improvement was shown with both methods: the treatment of the catalyst itself led, however, to a slightly higher selectivity. The best results obtained with each catalyst type are described in Table XIII.

TABLE XII

Influence of the Method Used to Treat the Catalyst with Basic Nitrogen-Containing Compounds

Catalyst	Basic nitrogen treatment	Activity (min)	C18:0	C18:1	C18:2	C18:3	% *trans*	% Solid at 10 C
Ref 24/8	No	64	9.0	44.6	32	1.8	15.3	13.3
	Amines added to the feed[a]	83.5	6.0	49.7	30	1.4	16.0	5.7
	Catalyst treatment with amines[a]	76.5	6.0	49.1	31	1.0	16.5	5.2
Ref 24/9	No	67.5	8.1	45.3	31.5	1.7	18.1	12.4
	Amines added to the feed[a]	83	6.7	50.7	29.8	1.4	16.1	7.1
	Catalyst treatment with amines[a]	75	5.7	50	30.5	1.0	18.0	4.8

[a] Coco primary amines have been used to obtain a N/100 Ni ratio of 10.

TABLE XIII

Results Obtained with the Most Selective Tested Catalysts

Catalyst	Activity (min)	C18:0	C18:1	C18:2	C18:3	% *trans*	% Solid at 10 C	% Dienes
Ni/TiO_2	53.5	6.0	48.3	30.8	1.0	18.5	4.0	0.4
Ni+ZrO_2/kieselguhr (ref 24/9) + lauryl primary amine added to the feed	77	5.7	49.8	30.0	1.0	17.0	4.2	0.1
Ni+ZrO_2/kieselguhr (ref 24/9) treated with coco primary amine	75	5.7	50.0	30.5	1.0	18.0	4.8	0.2

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Influence of Various Catalyst Poisons and Other Impurities on Fatty Acid Hydrogenation

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ABSTRACT

The effect of various impurities which reduce the activity of nickel catalysts during fatty acid hydrogenation has been studied. It is here proposed to divide the compounds which negatively influence the nickel-based fatty acid hydrogenation process into three categories, namely, catalyst poisons, inhibitors and deactivators, each group acting according to a different mechanism. The deleterious effect of typical catalyst poisons, such as S, N, P or Cl, is more or less independent of the chemical nature of the individual organic compounds containing these elements. There is good correlation between these element contents and the required nickel catalyst loading level. Other typical impurities present in technical fatty acids, such as oxidized fatty acids, soaps and water, also diminish the catalyst activity considerably. A number of experiments were designed to study the influence of various pretreatments of fatty acids on the catalyst loading levels needed for hydrogenation. In view of the high cost of nickel catalysts, considerable savings can be obtained by pretreatment of fatty acids prior to hydrogenation. Such pretreatment steps may include sulfuric acid washing, application of spent catalysts, and/or distillation. The most economical method will depend on local circumstances.

INTRODUCTION

The influence of catalyst poisons during hydrogenation of oils and fats in the presence of nickel catalysts has been studied in several investigations (1-6). Generally, all impurities reducing the catalyst activity have been termed "catalyst poisons," independent of their chemical nature or their origin. These impurities are either typical constituents of natural oils and fats or decomposition products or may be introduced during processing. These undesired compounds are not completely removed during oil refining and only to a small extent in the splitting process, which is normally the first step during fatty acid manufacture.

The fatty acid industry has an additional handicap because its raw materials are, in most cases, byproducts (acid oils) of edible oil refining or nonedible oils and fats, containing large quantities of impurities which adversely affect the hydrogenation of fatty acids. A split tallow fatty acid, for example, may contain the following catalyst poisons (in mg/kg): sulfur, 5-25; phosphorus, 10-50; chlorine, 10-100; and nitrogen, 200-600. Since industrial hydrogenation of fatty acids has to be as fast and as economical as possible, it is evident that impurities inhibiting the hydrogenation process play a very important role. Typical recommendations for the catalyst loading level in industrial hydrogenation of fatty acids of different quality are illustrated in Figure 1. This shows that, compared to edible oil hardening, large quantities of nickel catalyst are needed in fatty acid hydrogenation.

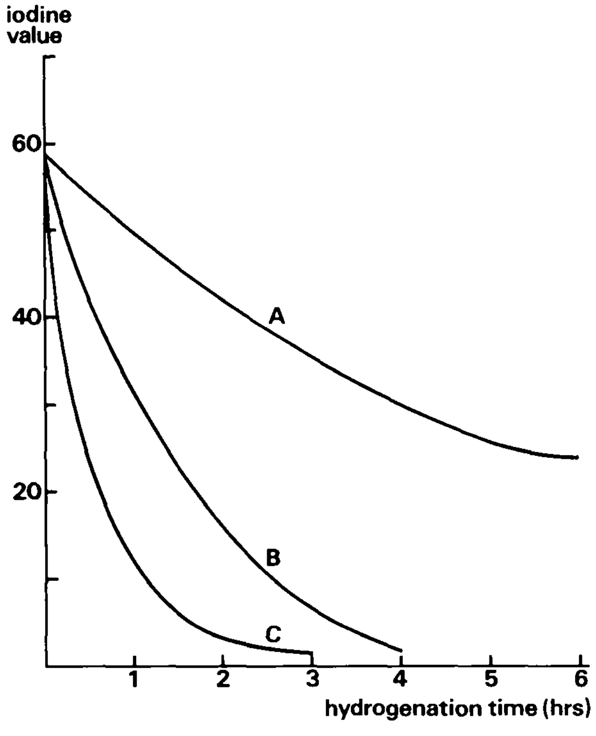

FIG. 1. Recommended catalyst loading levels in fatty acid hydrogenation. (A) Split fatty acid, 0.06% wt Ni; (B) split fatty acid, 0.24% wt Ni; (C) distilled fatty acid, 0.06% wt Ni.