Results

Table I presents data proving that the recovery of borax added to soap is quantitative within the experimental limitations of the method. The sprayed soap employed in the recovery experiments contained 3.8% H_2O, 61.2% anhydrous soda soap, 10.2% Na_2SiO_3, 4.7% $Na_4P_2O_7$, and 12.4% Na_2CO_3

Table II presents a comparison of values obtained in the analysis of various commercial products containing borax by the Poetschke method, and both the macro and semi-micro strontium methods.

Summary

A semi-micro procedure for the determination of borax in soap has been developed based on the fact that strontium metaborate is soluble in an excess of strontium chloride solution, whereas both strontium orthophosphate and silicate are quantitatively precipitated. The strontium metaborate is acidified and the liberated boric acid titrated to a-Naphtholphthalein in the presence of mannitol.

TABLE II
Determination of Borax in Commercial Soap Products

Product	Borax Present as % $Na_2B_4O_7 \cdot 10H_2O$		
	Poetschke Method (3)(4)	Macro Strontium Chloride Method	Semi-Micro Strontium Chloride Method
	%	%	%
Borax Soap Flakes A	0.77	0.87	0.89
Borax Soap Flakes B		0.76	0.76
Borax Soap Flakes C		1.53	1.50
Borax Bar Soap A	0.65	0.83	0.85
Borax Bar Soap B		1.62	1.59
Borax Bar Soap C		2.10	2.10
Borax Soap Powder A		0.67	0.67
Borax Soap Powder B	1.29	1.31	1.35
Borax Soap Powder C	2.35	2.36	2.45

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Partial Hydrogenation of Linseed Oil by a Continuous Process*

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Summary

Alkali refined linseed oil was partially hydrogenated, using both continuous and batch processes. The continuous process was carried out in a series of Votator machines, using Rufert nickel catalyst, pressures up to 145 psig. and temperatures up to 400°F.

The continuous hydrogenation of linseed oil under the most selective conditions possible, using the Votator equipment, shows little selectivity between the linolenic and linoleic acid radicals. A pronounced selectivity is observed between oleic and the more unsaturated acid radicals. Under selective conditions of hydrogenation of linseed oil about 31% of the hydrogenated linolenic acid radical is transformed into 9-15 linoleic acid while the remainder of the linolenic acid goes to oleic acid in either one or two steps.

Batch hydrogenation yields oils of superior non-yellowing characteristics over comparable oils prepared by the continuous process.

The hydrogenated linseed oils were tested in both clear and pigmented alkyds where they displayed superior non-yellowing characteristics over the original linseed oil and, in many instances, over that of soya bean oil.

The yellowing of oils and alkyds appears to be a function of both 1) the quantity of fatty acids more unsaturated than oleic present in the oil and 2) the ratio of the quantity of linolenic acid radicals to linoleic acid radicals present.

WHEN it looked as if the supply of soya bean oil would be sharply curtailed for use in paints and alkyds, it appeared possible to hydrogenate selectively the linolenic acid in linseed oil to linoleic acid without reducing the linoleic or oleic acids pres-

ent to more saturated acids to obtain a drying oil, with high linoleic acid content, with better drying qualities than soya bean oil, and with non-yellowing characteristics as satisfactory as soya bean oil.
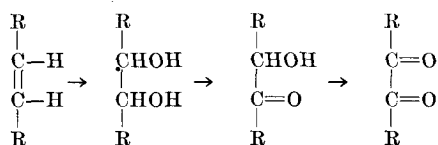
Yellowing

The yellowing of oil films or oil-containing vehicles upon aging is an important problem in the paint and varnish industry, especially in white paints and enamels. It has been shown that the free fatty acid content does not affect the yellowing tendency of an oil (1). The unsaponifiable matter, while affecting the yellowing, is not believed to be the prime cause. The relative susceptibilities of the various vegetable oils to yellowing appear to be more or less proportional to their degree of unsaturation (1, 7, 8, 9, 10). Oils which contain only small proportions of any fatty acids more unsaturated than linoleic (soya bean oil, poppyseed oil, dehydrated castor oil, etc.) are relatively free from this defect (2). Holman (6, 7, 8, 9) et al., believe that colored substances formed in the oxidation of fatty acids arise primarily from oxidation products of the fatty acids themselves and not from the oxidation products of trace substances present in natural fats.

Eibner and others believe that the yellowing of oils is a function of the amount of free or esterified a-linolenic and a-linoleic acid present. It is known that the hexabromide number is a quantitative measure of the linolenic content of an oil while the iodine number is a quantitative measure of the total unsaturation. Elm (1) and co-workers, however, have been unable to find any simple proportionality between these constants and the degree of yellowing in oils.
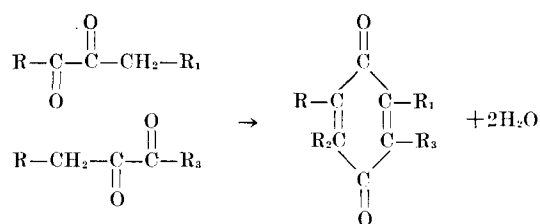
It is Scheiber's theory that the colored compounds are polyketones formed through oxidation of the double bonds.

$$
\begin{array}{cccc}
\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}{-}H & \underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}HOH & \underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}HOH & \underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}{=}O \\
\end{array}
$$

Elm and Standen (3) support Scheiber's theory and have shown that the diketostearic acid is definitely yellow whereas ketohydroxystearic acid is colorless. Elm (4) also believes that in studying the yellowing effect it is necessary to consider oxidation in conjunction with polymerization of the glycerides.

Prill (5) and O'Daniel and Parsons (6) showed the presence of diketones in partially oxidized fats containing fatty acids more unsaturated than oleic. A yellow color developed in alkaline solution was attributed to quinoid compounds formed by an aldol condensation of two diketone molecules, with subsequent dehydration.

$$
\begin{array}{c}
R{-}\overset{O}{\underset{\parallel}{C}}{-}\overset{\parallel}{\underset{O}{C}}{-}CH_2{-}R_1 \\
\\
R{-}CH_2{-}\overset{O}{\underset{\parallel}{C}}{-}\overset{\parallel}{\underset{O}{C}}{-}R_3
\end{array}
\rightarrow
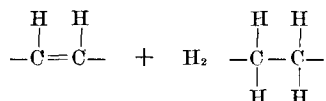\begin{array}{c}
\text{(ring structure)}
\end{array}
+2H_2O
$$

Holman (7, 8, 9, 10) *et al.*, in their work on the spectrophotometric studies of the oxidation of fats arrived at the following conclusions: a) the spectra of alkaline oxidized oleic acid or other fatty acids do not resemble the spectra of alkaline diketostearic acid, quinones, or diduroquinone; b) the alcoholic alkali color may in part be due to compounds derived from the unsaturated fatty acids which are closely related to the compounds obtained from chroman-5, 6-quinone by treatment of alkali; c) the alcoholic alkali color may in part result from other unsaturated carbonyl compounds which are oxidation products of unsaturated fatty acids.

The tendency to excessive yellowing of films from oils like linseed, which contain a large per cent of linolenic acid radicals and a high degree of unsaturation, has led to the extensive use in white paints and enamels of oils containing less linolenic acid and of a lower degree of unsaturated such as soya bean oil. If it is possible to remove or at least greatly reduce the linolenic acid content of linseed oil, a non-yellowing type of oil might result.

Hydrogenation

Hydrogenation (2) in modern oil and fat technology is confined mainly to the soap and edible fat industries. It is from the literature in these two fields that most of the information on catalytic hydrogenation was obtained for the present work.

The hydrogenation of an oil takes place with the addition of hydrogenation at the double bonds of the fatty acid chains:

$$
\begin{array}{ccc}
\overset{\overset{H}{|}}{C}{=}\overset{\overset{H}{|}}{C}{-} & + \quad H_2 & {-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{-}
\end{array}
$$

It is seen that the degree of hydrogenation in an oil is directly related to the iodine value which, conversely, can be used as a means of determining the extent of hydrogenation obtained with a given oil.

The process of hydrogenation requires a suitable temperature, gaseous hydrogen, liquid oil, and a solid catalyst. It is assumed that the hydrogen is first dissolved in the oil, and then the hydrogen-laden oil is brought into contact with the catalyst on whose surface the hydrogenation reaction occurs.

The catalyst employed in hydrogenation usually consists of nickel mounted on a porous, inert material. The catalyst is suspended in the oil during hydrogenation and removed by filtration at the end. Hydrogenation catalysts display a strong affinity for traces of impurities found in oils with a resulting "poisoning" effect. Sufficient catalyst must be employed to compensate for this effect.

The hydrogenation of fats and oils is a complicated reaction due to the glycerides involved. Hydrogenation has been found to be "selective" in that hydrogen tends to react first with the more unsaturated acids. However, hydrogenation of the more saturated acids does occur to some extent at the same time, the extent to which this occurs depends upon the conditions of hydrogenation. Selectivity in batch hydrogenation is favored by 1) high temperature, 2) low pressure, 3) low degree of agitation, and 4) high catalyst concentration (2). Another complicating factor is the tendency to form isomeric acids.

Bailey and Fisher (11) in their work found that under selective conditions of hydrogenation the relative reactivities of the unsaturated fatty acids toward hydrogen may be approximately represented by the following whole numbers: oleic—1, iso-oleic—1, iso-linoleic—3, linoleic—20, linolenic—40. Bailey and Fisher also found that the use of so-called non-selective conditions reduces the reactivity of linoleic and linolenic acids as a group compared to that of oleic and isolinoleic as a group but does not appreciably alter the relative reactivities of the two acids within the same group.

Van der Veen (12) subjected hydrogenated methyl linolenate to ozonolysis and concluded from the nature of the breakdown products that hydrogenation had caused saturation of the 12:13 bond yielding 9-15 methyl linoleate. Lemon's (13) investigation of the course of hydrogenation of linseed oil by the spectral method of Mitchell, Kraybill, and Zscheile (14) also indicated that linolenic acid is converted to an isomeric linoleic acid. In a typical hydrogenation Lemon found that the concentration of isomeric acid increased to a maximum of 18% of the total fatty acids at an iodine number of 120.

It is generally agreed that, while the hydrogenation of fatty acids is fairly selective, there is much less selectivity with respect to the glycerides. It has been reported that the selectivity between linolenic and linoleic is less in linseed oil than in soya bean oil (11).

Hydrogenation processes may be divided into two general classes, namely, a) the batch process, and b) the continuous process. According to A. E. Bailey (2) the continuous process produces a hydrogenated product quite different in composition and characteristics from the batch process. Continuous hydrogenation also is characterized by a lack of selectivity.

As the hydrogenation of an oil proceeds, most of the characteristics of the oil which do not depend upon the unsaturation are substantially unchanged. A bleaching effect, however, is usually noted. The refractive index and the iodine value, two charac-

teristics which depend upon the unsaturation, are both reduced by hydrogenation (2). The relationship between refractive index and iodine value is very nearly the same for most vegetable oils. Because of this the refractive index can be used as an indication of the iodine value in a hydrogenated oil and thus serve as a means of control during the hydrogenation reaction.

Apparatus

In attempting to hydrogenate selectively the linolenic acid in linseed oil to linoleic it was decided to carry out the hydrogenation reaction, using a new continuous processing method developed by the Votator Division of the Girdler Corporation.

The continuous equipment set-up, as illustrated by the flow diagram in Fig. 1, consisted of the following:

1. Slurry Tank: This is the tank in which the linseed oil, catalyst, and filter aid were mixed.

2. Circulating Pump: This pump supplied slurry to the pressure pump. The excess was returned to the slurry tank, via the recirculating line, thus keeping the slurry continuously in an agitated state.

3. Pressure Pump: This pump supplied slurry to the Votators and maintained the desired pressure in the system.

4. Heating Votator: This was the heat exchanger used to bring the slurry up to reaction temperature. The heating medium used was either steam or Dowtherm, depending on the temperature desired.

5. Hydrogenation Votator: This vessel was used to mix the gaseous hydrogen and slurry, and as the reaction vessel.

6. Gaseous hydrogen was obtained from cylinders, passed through a rotameter and into the Hydrogenation Votator.

7. Cooling Votator: This was a heat exchanger for cooling the hydrogenated oil slurry down to room temperature.

8. Discharge Pump: This pump was used to remove the oil slurry from the system and to regulate the rate of flow through the system.

The Votator machine, Fig. 2, a development of The Votator Division of the Girdler Corporation, is basically a heat exchanger operated under superatmospheric pressure on the product side and consisting of a jacketed cylinder within which a shaft or rotor turns. It is characterized by a high ratio of heat exchange surface to volume of product under treatment. The annular space between motor and cylinder wall is quite small. The conventional rotor is equipped with a set of scraper blades, which, as the rotor turns, scrape the sides of the cylinder destroying the liquid film on its inner surface, thereby removing a large loss-factor in the heat transfer.

Several comparative runs were made by the batch process to serve as a check on the continuous process. The batch hydrogenation was carried out in a conventional type, vertical autoclave equipped with vertical agitator, hydrogen gas inlet line, temperature and pressure measuring devices, and a connection for applying vacuum and relieving pressure.

Materials

The slurry used in the hydrogenation work consisted of the following:

97% Varnish Linseed Oil—Alkali refined ($n_d^{25} = 1.4789$).

2% Rufert Catalyst composed of 25% activated nickel and 75% hydrogenated soy bean oil.

1% "Celite" as filter aid.

The discharge rate was held at approximately 20 pounds of oil per hour, which allowed about three minutes holding time in the Votator machines.
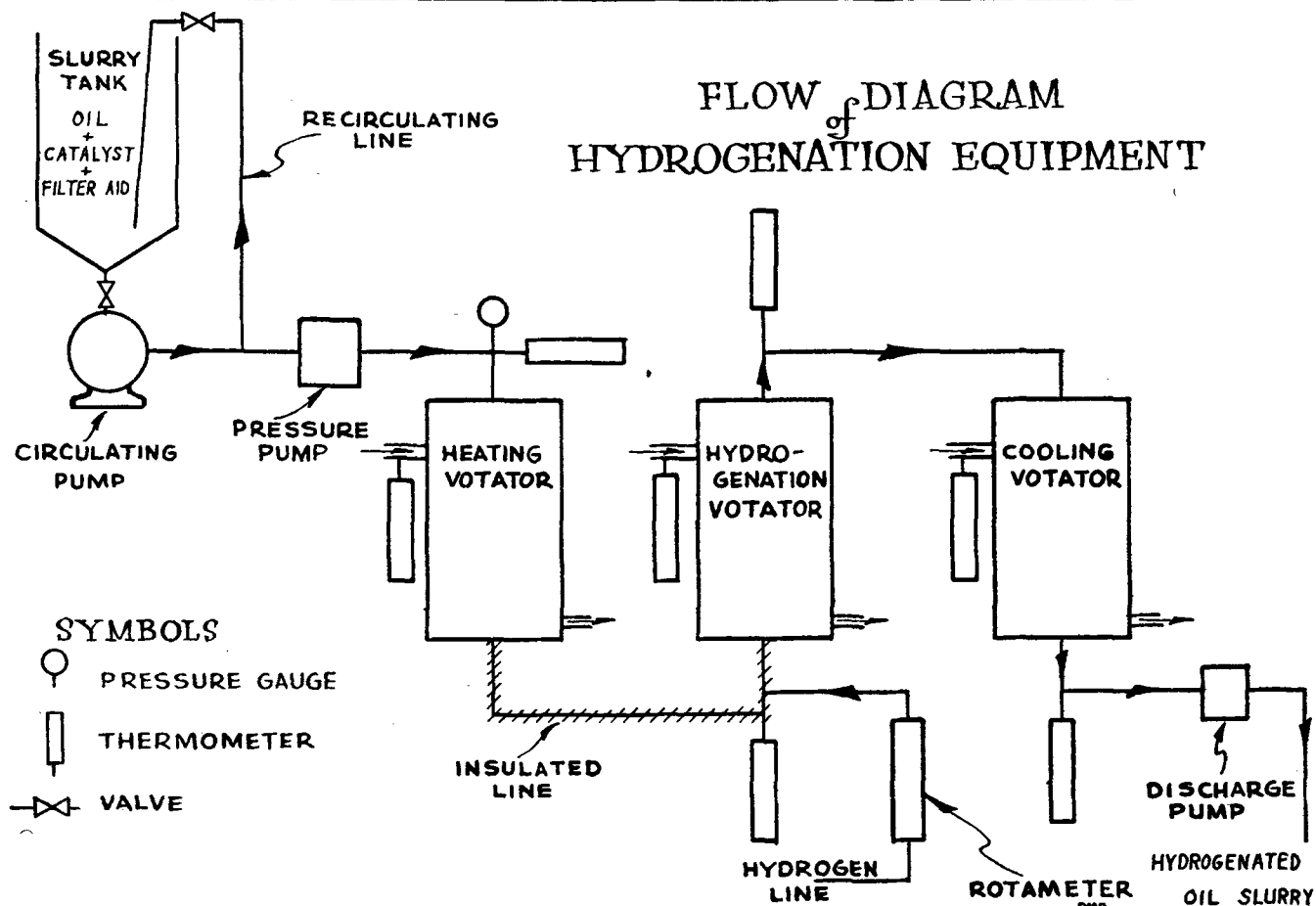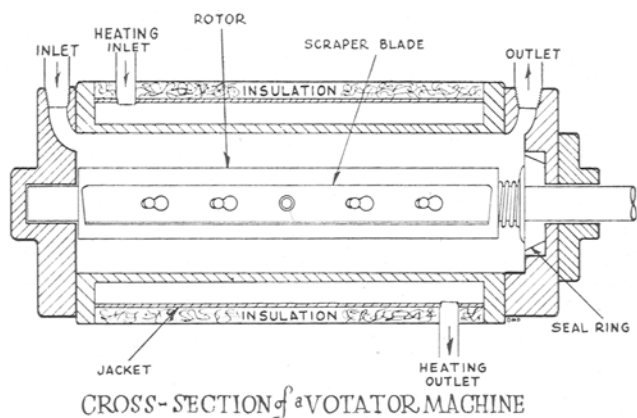

Fig. 1.

CROSS-SECTION of a VOTATOR MACHINE

FIG. 2.

Notes on Procedure

The Votator machines were of 4″ cylinder diameter.

The concentration of catalyst was set at 0.5% activated nickel (2% Rufert catalyst) to insure sufficient catalyst for complete reaction.

In lieu of determining iodine numbers, the refractive index was used as a means of control. The refractive index drops approximately 11 points in the fourth decimal place for every 10-point drop in iodine number (2).

Hydrogenation Data

The conditions of the various hydrogenation runs are given in Tables I and II.

Run No. 2 indicated that for a given temperature oil rate and hydrogen input there is an optimum minimum pressure for satisfactory hydrogenation in the Votator machine. (See Graph I). At pressures below 50 psig., the free hydrogen noted in the discharge product accounts for the incomplete hydrogenation. No satisfactory explanation can be given for the apparently incomplete hydrogenation at the higher pressures.

Run No. 3 showed us that for satisfactory hydrogenation to an approximate iodine number of 100, the optimum minimum pressure is about 100 psig. at 325°F. (See Graph I).
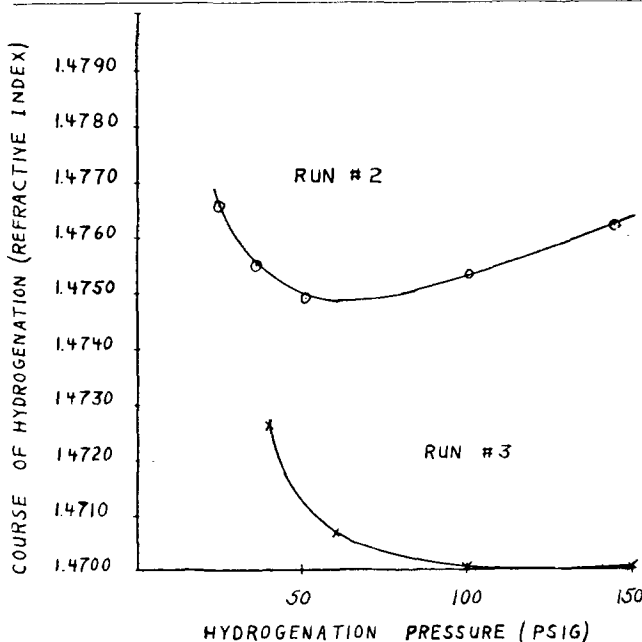
GRAPH I. Difference in the refractive index (a measure of the iodine number) of linseed oils hydrogenated continuously in a Votator machine at 325°F., with constant hydrogen input, but at different pressures.

Run No. 2—Sufficient H_2 for I_2 No. = 145 (n_D = 1.4750) if all reacts.

Run No. 3—Sufficient H_2 for I_2 No. = 100 (n_D = 1.4699) if all reacts.

TABLE I

Continuous Hydrogenation of Linseed Oil

Run and Sample No.	Oil Slurry Flow-rate lb./hr.	Rotor Speed (r.p.m.)	Remarks	Reaction Temp. (°F.)	Reaction Pressure (psig.)	n_d^{25}	Esti-mated Iodine No.	Deter-mined Iodine No.	Remarks
2-A	20	1,000		330	145	1.4763	158		
2-B	20	1,000	Hydrogen rate ∿ to 25% xs H_2	330	100	1.4753	150		
2-C	20	1,000	over that to react with (1)	330	50	1.4749	146		
2-D	20	1,000	double bond in linolenic	328	35	1.4754	151		Free hydrogen in discharge
2-E	20	1,000		325	25	1.4766	160		Free hydrogen in discharge
3-A	20	1,000		325	150	1.4701	100		
3-C	20	1,000	Hydrogen rate ∿ to reduce I_2	325	100	1.4700	100		
3-D	20	1,000	No. to 100	325	60	1.4707	107		Free hydrogen in discharge
3-E	20	1,000		320	42	1.4727	126		Free hydrogen in discharge
4-	20	1,000		275	108	1.4758	152		Spasmodic discharge
4-	20	1,000	Hydrogen rate ∿ to reduce I_2	275	150	1.4730	128		Spasmodic discharge
4-A	20	1,000	No. to 100	280	190	1.4703	103		Free hydrogen in discharge
4-B	20	1,000		300	170	1.4701	101		Slight free hydrogen in discharge
5-A	20	1,000	Moderately selective conditions	323	60	1.4764	160	158	
5-B	20	1,000	Moderately selective conditions	323	60	1.4753	150	155	
5-C	20	1,000	Moderately selective conditions	320	61	1.4746	142		
5-F	20	1,000	Moderately selective conditions	325	62	1.4733	131	134	Free hydrogen in discharge
5-G	20	1,000	Moderately selective conditions	320	65	1.4723	121	125	Free hydrogen in discharge
6-B	20	1,000	Non-selective conditions	300	170	1.4768	162		
6-C	20	1,000	Non-selective conditions	300	170	1.4756	152		
6-D	20	1,000	Non-selective conditions	300	165	1.4741	138		
6-E	20	1,000	Non-selective conditions	300	163	1.4730	129	129	Free hydrogen in discharge
6-F	20	1,000	Non-selective conditions	300	170	1.4721	121	124	Free hydrogen in discharge
7-	20	600	Highly selective conditions	400	75	1.4738	135		Spasmodic discharge
7-	20	600	Highly selective conditions	400	115	1.4720	120		Spasmodic discharge
7-	20	600	Highly selective conditions	400	140	1.4706	107		Spasmodic discharge
7-	20	600	Highly selective conditions	400	154	1.4700	100		Spasmodic discharge
7-A	20	600	Highly selective conditions	415	145	1.4710	110	118	Free hydrogen in discharge
7-B	20	600	Highly selective conditions	405	135	1.4746	142	147	
7-C	20	600	Highly selective conditions	410	143	1.4722	120	128	Free hydrogen in discharge
7-D	20	600	Highly selective conditions	405	137	1.4730	128	134	

In run No. 4 it was found that satisfactory hydrogenation could not be obtained at 275°F. without going to comparatively high pressures. At the lower pressures the hydrogen did not readily dissolve in the oil as indicated by the spasmodic discharge.

Runs No. 5, 6, and 7 give a comparison of linseed oil samples hydrogenated by the continuous process under moderately selective conditions, non-selective conditions, and most selective conditions, respectively.

It is noted that our use of the refractive index method of control of iodine values apparently estimated values about five units lower than the determined values in most cases.

TABLE II
Batch Hydrogenation of Linseed Oil

Sample	Reaction Temp. (°F.)	Reaction Pressure (psig.)	Time of Hydrogenation (min.)	Product		
				n_d^{25}	Estimated Iodine No.	Determined Iodine No.
9-A	400	48	17	1.4725	124	127
9-B	400	15	52	1.4723	122	125
9-C	300	50	35	1.4720	120	124
9-D	328	62	18	1.4724	123	128
9-E	400	62	11	1.4715	115	120
9-F	300	62	21	1.4722	121	127

The speed of agitation was 250 r.p.m.

Analysis

Representative samples of the hydrogenated oils along with a sample of untreated linseed oil and one of untreated soya bean oil were analyzed by General Mills, Inc., according to the methods suggested by Bailey and Fisher (11), with the exception that per cent saturated acids were determined by the low temperature crystallization method instead of by the Bertram method. The linolenic and linoleic acids were determined by the spectral method. The total oleic and isolinoleic acids were estimated according to the preceding determinations and the iodine number of the oil. The results of the analysis are summarized in Table III.

TABLE III
Analysis of Hydrogenated Oils

Sample No.	Det. I.V.	Det. %l3(a)	Det. %l2(b)	Calc. % iso-l2 (c)	Calc. % ol (d)	Det. % Sat.
Untreated linseed	181.8	50.0	14.0	3.0	25.0	8.0
6-E	130.4	17.6	12.9	14.0	44.0	11.5
6-F	122.5	15.3	13.0	12.5	44.5	14.7
7-A	117.6	9.9	9.8	15.6	55.5	9.2
7-C	125.3	13.6	11.6	16.6	47.6	10.6
7-D	134.1	18.0	12.9	17.3	40.5	11.3
9-B	124.0	12.7	11.9	15.3	51.2	8.9
9-D	128.2	14.3	13.3	18.6	41.7	12.1
9-F	125.3	12.8	13.5	20.4	39.1	14.2
9-E	119.3	9.9	10.9	18.3	50.2	10.7
Untreated soya bean	134.1	8.6	52.0	0.0	25.9	13.5

NOTES:
(a) l_3 = linolenic.
(b) l_2 = linoleic.
(c) iso-l_2 = isolinoleic (linoleic acid which does not analyze by spectral method.) (Probably 9-15 linoleic.)
(d) ol = oleic and iso-oleic.

Discussion

The change in fatty acid composition that occurs during the selective hydrogenation of linseed oil in the Votator machine is shown graphically in Graphs II and III. The graphs were prepared, using the above analytical data obtained by General Mills, Inc. on untreated linseed oil and on the samples from run No. 7 in which linseed oil was hydrogenated continuously under selective conditions.
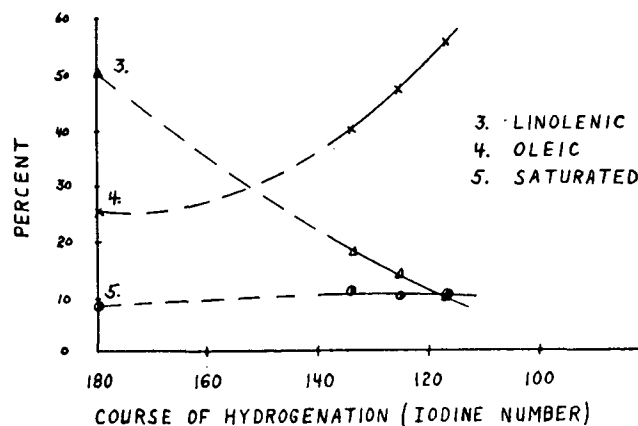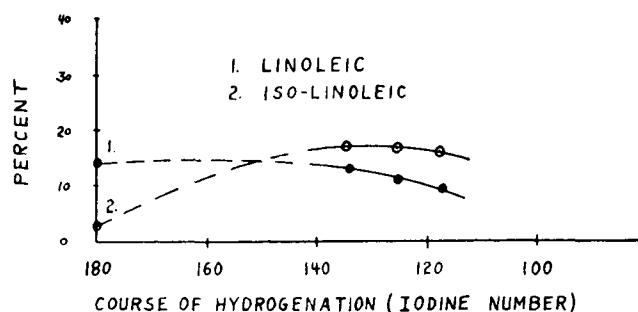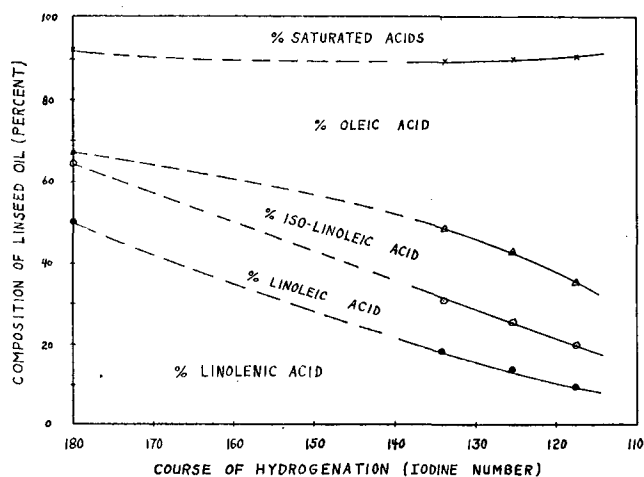

GRAPH II. Progressive change in the fatty acid composition of linseed oil during selective hydrogenation in a Votator machine.

From the analytical data and the graphs it is seen that the problem of selectively hydrogenating the linolenic acid radical of linseed oil to linoleic acid without reducing the linoleic acid to more saturated acids was not solved. Very little selectivity is observed between the linolenic and linoleic acid radicals. A pronounced selectivity is observed between oleic and the more unsaturated acid radicals. Under selective conditions of continuous hydrogenation of linseed oil, the relative reactivities of the unsaturated fatty acid radicals toward hydrogen were found to be approximately represented by the following whole numbers: oleic—1, linoleic—26, and linolenic—38. This compares with values of 1:23:40, reported by Bailey and Fisher (11) for the fatty acids of oleic, linoleic and linolenic, respectively.

It is also seen that in the hydrogenation of linseed oil, a relatively large percentage of 9-15 linoleic acid radicals is formed.

Under selective conditions of continuous hydrogenation the maximum percentage of 9-15 linoleic acid radicals obtained was 17.3% at an iodine value of 134. With batch hydrogenation the maximum percentage of 9-15 linoleic acid radical obtained was 20.4% at an iodine value of 125. These figures compare with a maximum concentration of isomeric acid of 18% at an iodine value of 120 as found by Lemon (14). The hydrogenated linolenic acid which did not go into 9-15 linoleic acid was apparently further hydrogenated on to oleic acid.

Only slight differences were noted in the selectivity between the batch process and the continuous process using the Votator machine. From the quantity of poly-unsaturated acid radicals in the final hydrogenated linseed oil compared to that in soya bean oil, it might be concluded that the hydrogen-

GRAPH III. Progressive change in the total composition of linseed oil on selective hydrogenation in a Votator machine.

ated linseed oil will display slightly poorer air drying characteristics than soya bean oil, as was the case.

Tests in an Alkyd

Representative samples of the hydrogenated oils were used to prepare 40% oil-modified alkyds. Films, 0.004 inches in thickness, were applied to white Cararra glass plates, without addition of drier, and baked one hour at 300°F. The panels were then removed from the oven and compared for color retention. The results along with the data on the alkyds are given in Table IV.

From Table IV it is seen that all of the hydrogenated oils tested showed up better than linseed oil in the color retention properties (non-yellowing) of the modified alkyd; and all except 6F, which was obtained under non-selective conditions, proved to be better than soya bean oil in non-yellowing characteristics. It is interesting to note that oils hydrogenated by the batch process imparted the best color retention properties to the modified alkyd, and also produced alkyds with the lightest color.

The improvement in the non-yellowing characteristics of linseed oil upon hydrogenation cannot be attributed to the decrease in the linolenic acid content since in all the hydrogenated oils the final percentage of linolenic acid is greater than that found in soya bean, yet the non-yellowing is superior.

For example, take sample 7C. This is a sample of linseed oil hydrogenated continuously under selective conditions in the Votator machine. Sample 7C con-

tains 58% more linolenic than does soya bean oil; the soya bean oil contains 4.5 times as much linoleic as sample 7C; sample 7C has a total of 41.8% of acids more unsaturated than oleic; soya bean oil has 60.6% of acids more unsaturated than oleic; the soya bean oil-alkyd film has poorer color retention than the hydrogenated oil-alkyd film. Thus, although linolenic acid yellows much worse than linoleic, the 58% extra amount of linolenic acid present in sample 7C over that in soya bean oil is not enough to cause as much yellowing as apparently is caused by the 4.5 times more linoleic that was in the soya bean oil.

It is noted that the total unsaturation in the hydrogenated oils tested is less than that of soya bean oil. It has been stated (1) that the susceptibility of drying oils to yellowing is more or less proportional to their degree of unsaturation.

The better color retention of the oils hydrogenated by the batch process may be due to the slightly better selectivity encountered in batch hydrogenation though the difference seems much too small to be the only cause. It may be partially due to the decreased formation of color bodies in the alkyd cook as shown by their lighter color though why this should be so is not clear.

Tests in a Mill White Paint

Representative samples of the hydrogenated oils were used to prepare 60% oil-modified alkyds which then were incorporated into a mill white paint of the following formulation:

Material	Parts by weight
TiO₂—Rutile	285
ZnO—French process	95
No. 103 Castung oil	20
Hydrogenated oil	604
Mineral spirits	66
Turpentine	21
Cobalt naphthenate (6% Co.)	7
Lead naphthenate (24% Pb.)	3

The paint was brushed out on panels and air dried. Table V gives the results on color retention of the air-dried films after 9 months exposure. When the above panels were prepared, it was noted that the air drying characteristics on those formulated with the hydrogenated oil modified alkyds were uniformly poor. This was expected from the low iodine numbers.

The color retention results with the mill white enamels checked fairly close with those obtained on the baked clear alkyd films. All the enamels formulated with hydrogenated oil-modified alkyds displayed

TABLE IV

	Oil Data		Alkyd Data					
Sample No.	Conditions of Hydrogenation	Cooking Temp. (°F.)	Cooking Time (hrs.)	Visc. (Gardner)	Acid No.	Color (Gardner)	% Solids	Color Retention (a) when baked 1 hour at 300°F.
Untreated linseed		390	9	O	8.12	9	47.2	9(e)
5-F	Continuous mod. selective	348	16.5	M	9.5	10	50.4	6(c)
5-G	Continuous mod. selective	390	7	N-O	11.2	9	50.1	5(c)
6-F	Continuous non-selective	370	11.75	O	6.94	9	49.2	8(d)
7-C	Continuous highly selective	390	7	N-O	8	6	50.4	4(c)
9-B	Batch highly selective	390	7.5	M-N	8.96	6	51.1	1(b)
9-E	Batch mod. selective	390	9.25	O	11.9	4-5	49.5	2(b)
9-F	Batch non-selective	390	6	O	8.75	5	49.1	3(b)
Untreated soya		390	8	N	9.65	7	49.3	7

NOTES:

(a) 1 on the color retention scale is the best rating.
(b) Samples 9-B, 9-E, and 9-F are by far the best in color retention.

(c) Samples 7-C, 5-F, 5-G are slightly better than soya bean oil.
(d) Sample 6-F is slightly worse than soya bean oil.
(e) Linseed oil is by far the worst in color retention.

TABLE V

Oil Data		Alkyd Data				Mill white data color retention of (a) brushed out films after 9 months' air dry
Sample No.	Conditions of Hydrogenation	Visc. (Gardner)	Acid No.	Color (Gardner)	% Solids	
Untreated linseed		Y	7.8	8	67.8	11
Untreated soya bean		Y plus	6.9	6-7	73.2	5
7-B	Continuous highly selective	X	8.6	7	68.5	6
5-B	Continuous mod. selective	W-X	1.1	9	68.0	8
5-C	Continuous mod. selective	Y	8.4	10	69.0	7
5-F	Continuous mod. selective	Y plus	11.9	10	71.3	10
6-D	Continuous non-selective	X-Y	12.7	9-10	70.1	9
6-F	Continuous non-selective	Y	13.0	11	69.3	2
9-C	Batch mod. selective	Z	11.2	7-8	70.4	4
9-D	Batch mod. selective	Z	2.3	7	69.0	1
9-F	Batch non-selective	Y	9.1	8-9	69.2	3

NOTE: (a) 1 on the color retention scale is the best rating.

superior non-yellowing characteristics in comparison with the standard enamel containing linseed oil modified alkyd.

Also in line with the color retention results obtained on the baked clear films it will be noted that the oils hydrogenated by the batch process gave the best non-yellowing characteristics, even better than soya bean oil.

Conclusions

The continuous partial hydrogenation of linseed oil under the most selective conditions possible, using the Votator machine, shows little selectivity between the linolenic and linoleic acid radicals. A pronounced selectivity is observed between oleic and the more unsaturated acid radicals.

In the continuous partial hydrogenation of linseel oil about 31% of the hydrogenated linolenic acid radical is transformed into 9-15 linoleic acid, the remainder going to oleic acid in either one or two steps.

All the hydrogenated linseed oils tested in both the clear and pigmented alkyds displayed superior non-yellowing characteristics over the original linseed oil, and in many instances over that of soya bean oil. This superiority in non-yellowing qualities cannot be attributed entirely to the decrease in the linolenic acid radical content since all the hydrogenated oils contained a larger per cent of linolenic acid than did soya bean oil. It is noted that the percentage of acids more unsaturated than oleic in the tested hydrogenated linseed oils is less than that in soya bean oil. There is another possible explanation of this difference in yellowing; namely, that the 9-15 linoleic acid may have a much more decreased tendency to yellow than the 9-12 isomer.

Batch hydrogenation yields oils of superior non-yellowing characteristics over comparable oils pre-pared by the continuous process. It can be postulated that the yellowing of oils is a function of both 1) the quantity of fatty acids more unsaturated than oleic present in the oil and 2) the ratio of the quantity of linolenic acid radicals to linoleic acid radicals present in the oil.

Acknowledgment

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