

CORN OIL AND ITS HYDROGENATION.*

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CORN OIL, AS A SUBSTITUTE FOR OLIVE AND COTTONSEED OIL.

In the investigation of this oil, the physical properties, saponification value, iodine absorption number were taken, which were as follows:

The congealing point, composition and refractive index of the three oils may be seen from the subjoined table:

	Corn oil.	Cottonseed oil.	Olive oil.
Congeaing point.....	—10 to —15° C.	—0 to —5° C.	—0 to —5° C.
Composition:			
Solid fatty acid.....	27%	32%	15%
Liquid fatty acid.....	73%	68%	85%
Refractive Index by Strohmert at 15.5° C.....	1.4768	1.4743	1.4698

The following classes of preparations were experimented upon for substitution of corn oil for olive oil: Liniments, ointments, cerates, plasters, oleates.

The determination of the constants of corn oil, obtained from the Douglas Company, Cedar Rapids, Iowa, and made by Mr. Lackey, my associate in experimental work, were as follows:

Number.	Determination.	Values.
1	Saponification value.....	188-191
2	Iodine value (Hanus).....	115-119
3	Specific gravity.....	0.920-0.924
4	Free fatty acids (crude oil).....	4.4%
5	Free fatty acids (refined oil).....	1.05%

The Determination.—It seemed to us that the hydrogenated product might well be used in place of solid fats in various preparations and this idea led to the study of hydrogenation of corn oil. It may not be out of place here to state the general principles of hydrogenation.

Generally speaking, we may say that any liquid fat may be hydrogenated under the proper conditions. The ease with which hydrogenation takes place depends on several properties of the oil, as the degree of unsaturation (indicated by the iodine value). The higher the iodine value, the longer hydrogenation must proceed before the stearin stage is reached—which point is easily understood when we remember that a high iodine value will mean the presence of highly unsaturated bodies as linolic acid, linolenic acid or their glycerides. The ease with which an oil is hydrogenated is also affected by impurities in the oil, which may affect or poison the catalyzer.

From the simplicity of the reaction, hydrogenation would seem a very simple process. But the problem is far from simple as olein or oleic acid, under the methods first tried, resisted to any material extent the invasion of hydrogen into its structure. In fact, this was not successfully accomplished until the metallic catalyzers, or hydrogen carriers, were tried.

But the process to-day has reached such a degree of perfection that plants for

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the commercial production of "hardened" oils have sprung up all over the world. The extent of the commercial importance of this industry is well stated by Ellis when he says, "So eagerly has the oil handling world lent itself to the idea, that already the stearin market has lost its firmness and much speculation is rampant as to the nature of price re-adjustments, which perhaps are on the way. Unquestionably, hydrogenated or hardened oil has taken its place in the oil market as a staple product."

A general method may be described as follows: The process consists of the use of a suitable catalyzer; for example, a freshly precipitated nickel oxide is reduced, by passing a current of hydrogen through it, to a metallic state. This is carried on at a temperature of 360°C . The finely divided metallic nickel constitutes the catalyzer in question. The nickel, reduced as above, is dried in an at-

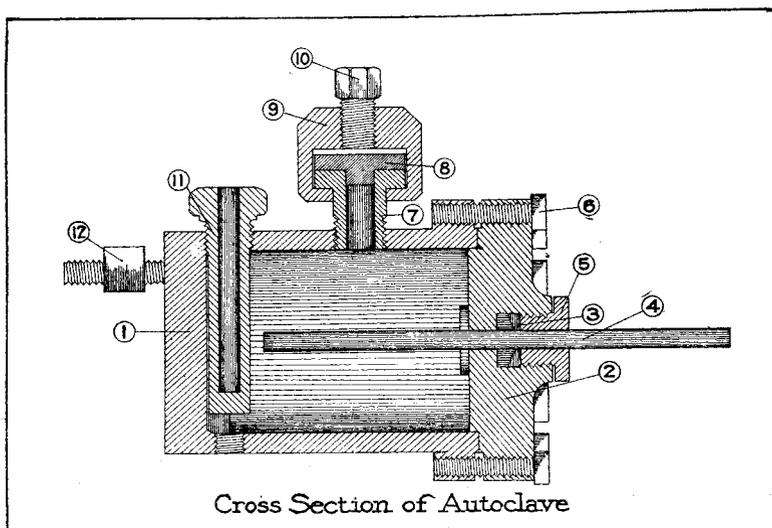


PLATE NO. II

- 1.—Main cylinder used to contain the oil under investigation.
- 2.—Cap or cover for cylinder No. 1—fitted to the cylinder with ground joint and held in place by twelve $\frac{1}{4}$ inch cap screws (6).
- 3.—Packing ring to secure gas-tight packing around rotating shaft.
- 4.—Driving shaft fitted with shoulder fitted against cap with ground joint. Either wire gauze agitator or balloon flask can be mounted on the driving shaft.
- 5.—Packing nut.
- 6.—Cap screws with No. 2.
- 7.—Charging hole through which oil and catalyst may be introduced into autoclave.
- 8.—Cap for charging hole. Fitted to No. 7 with ground joint.
- 9.—Clamp used to hold No. 8 in place.
- 10.—Set screw in clamp No. 9.
- 11.—Thermometer well.
- 12.—Tee for connecting to autogenor or hydrogen cylinder.

mosphere of hydrogen and is brought in contact with the oil to be hydrogenated, care being taken that it shall not come in contact with the action of the air during the process. The mixture of oil and nickel is then brought in close contact with hydrogen through a tall cylindrical tank and in still closer contact by an adjustment to the apparatus, which causes the mixture of oil, catalyzer and hydrogen to flow through a narrow tube, the whole being kept at a temperature of from 175° to 190°C . The pressure is maintained in hydrogenation from one atmosphere, or less, to 25 pounds. Any excessive pressure is liable to cause leakage of hydrogen which is difficult to keep from issuing through the tightest of vessels. The pres-

sure used is regulated for different oils, some requiring more than others for proper hydrogenation. After the hydrogenation is effected, the mixture is pumped into a tank, heated by steam, then conducted to a filter press where the catalyzer is removed by filtration and the oil permitted to harden.

The apparatus used by us was constructed for experimental purposes only, where any quantity from 15 Cc. of oil to about 250 Cc. could be hydrogenated.

The experimental work on corn oil consisted of, in the first place, the degree of hydrogenation (indicated by melting point and iodine value) under different conditions of time, temperature, pressure, catalyzer content, etc.

The next investigation was concerned with the problem of a catalyzer, determining the rate of reaction of nickel oxide catalyzer which has undergone various degrees of reduction, in the process of hydrogenation.

It was found that the most favorable condition for the hydrogenation of corn oil, with our apparatus, was a pressure of 50 pounds, running the apparatus, or continuing the hydrogenation, for six or seven hours at a temperature of 200° C. This gave a product which had a melting point of about 36° C.

It is a question of interest as to whether hydrogenated corn oil could compete commercially with the other hydrogenated oils. In this connection we would observe that at present the price of corn oil is slightly below that of cottonseed oil. Therefore, since cottonseed oil is being successfully hardened and sold, we should be able to do the same thing with corn oil. In the second place, we may consider the ease of hydrogenation. We have run some comparative tests on hydrogenation between corn oil and similar oils of about the same iodine value and, as is seen from the following table, we may judge corn oil to be as capable of hydrogenation as any similar oil. The difference in melting points may be attributed to the fact that cottonseed oil has lower iodine value than corn oil, but, on the whole, the agreement is quite good.

Cottonseed oil.		Corn oil.	
Time.	Melting point.	Time.	Melting point.
6 hours	35° C.	5½ hours	31° C.
10 hours	39° C.	7 hours	34° C.
7 hours	35° C.	7 hours	33° C.
3 hours	29° C.	3½ hours	23° C.

It should be stated that when nickel oxide is used a trace of this is present in the finished product, about 0.006 percent. Such an amount would be regarded as objectionable for edible purposes although many investigators claim that nickel in minute amounts in foods has no toxic effect. Nickel-lined vessels have been used for years, and food prepared in them contains two or three parts per million, yet no injurious effects have resulted. This is as much as the average oil prepared by nickel catalyzers contains.

The presence of this amount of nickel would certainly not interfere or be objectionable in making most of the unctuous preparations. The one merit this hydrogenated product seems to have is its keeping quality. We believe we have proven the keeping qualities of hardened corn oil since we have samples of the hydrogenated product which have kept their sweet flavor and have not become the least rancid in over a year. This hydrogenated product has kept better even than a similar sample of cottonseed oil although it was subject to various changing conditions such as light, oxidizing action of the air and great changes of temperature.

It is worthy of note, in closing, that besides edible products, hydrogenated oils may be used for any purpose to which solid fats are put, as soap making, lubricants, etc.

Since liquid fats are essentially cheaper than natural fats and since it is possible to cheaply harden them to any desired consistency, hydrogenation is rendered especially attractive to soap manufacturers. The soap manufacturer has now at his disposal the means of utilizing low grade material in substitution for more costly stock. It is now possible to make hard soap, with the aid of hydrogenation, from oils which formerly gave only soaps of soft consistency.

According to the Japanese chemist, Tsujimoto, the odor of fish oil is due to a very unsaturated fatty acid called clupanodonic acid, $C_{18}H_{28}O_2$, and not to so-called impurities as is commonly supposed. Thus we see that by the addition of eight hydrogen atoms it is possible to produce stearic acid. When hardened down to an iodine number of 50, fish oil has the consistency of hard tallow and has lost all of its odor of fish and, in fact, has destroyed most of the fishy taste. Therefore, this would make a satisfactory soap stock and hardened fish oil is, in fact, extensively used in Europe for soap making.

Not so very much work has been done on the utilization of hardened oils for soap making in this country, but in Europe the industry is becoming quite extensive.

For a detailed discussion of soap making, including formulae, etc., utilizing hardened oils, the reader is again referred to Ellis' book, "The Hydrogenation of Oils."

On the subject of hardened oil for lubricants, it might be said that the physical and chemical properties of hardened oils, especially fish oil, indicate that these products could be well used in the manufacture of lubricants.



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(Joseph, Baron Lister)

Born in Upton Lane, West Ham, England, April 5, 1827. Died February 10, 1912, at Walmer; buried in Hampstead (London) cemetery, where a plain, grey granite slab covers the grave.



IGNAZ PHILIPP SEMMELWEIS, M.D.

Born Ofen, Budapest, July 1, 1818. Died August 13, 1865; buried in Budapest where a monument has been erected over his grave by this municipality. The photograph is from *Semmelweis' Gesammelte Werke* by Dr. Tiberius von Györy