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Heat Polymerization of Safflower Oil[1]

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FOR some time the oil chemist has been intrigued by the potentialities of safflower seed oil in the field of drying oils and organic coatings (1, 2). However only during the last 12 months has safflower oil appeared on the competitive American vegetable oil market in sufficient quantity to stimulate interest in its commercial usage on a national scale. In view of the interest in this relatively new oil, a study was undertaken in an attempt to obtain some basic information regarding its heat bodying characteristics under practical conditions. With the wealth of information on the bodying of linseed oil under various conditions, it was felt that similar practical work on safflower oil, even though limited in scope, would be of general interest and value to the industry.

A study was made of the polymerizing rate of safflower oil at temperatures of 575°, 585°, and 595°F. A commercial grade of safflower oil was processed in 1,000-gallon batches, and similar runs were made with linseed and soybean oils for the purpose of comparison. All cooks were made in the same kettle under identical conditions. In each case the oils were heated to 200°F.; at this point a vacuum of about 29½ inches and a mild inert gas sparge were applied to the kettle while heating was continued to gain polymerizing temperature. This temperature was maintained until the desired viscosity was reached, at which time the oil was cooled to 300°F. and vacuum released. In each cook samples were taken at intervals, and a sufficient amount of each sample was retained in order that accurate determinations of acid number, viscosity, iodine number, and refractive index could be made.

The safflower oil used in this study was a shipment from the 1950 California crop. The constants of this oil, together with the constants of the linseed and soybean oils used, are shown in Table I. It should be noted that the iodine value of the linseed oil, though acceptable, is on the low side of commonly used specifications. However the rate of polymerization was normal and did not reflect the low iodine number.

The equipment used to obtain the data for this study was a commercial installation, comprising a 1,200-gallon stainless steel process kettle of recent design (Fig. 1). It is equipped for use of high vacuum

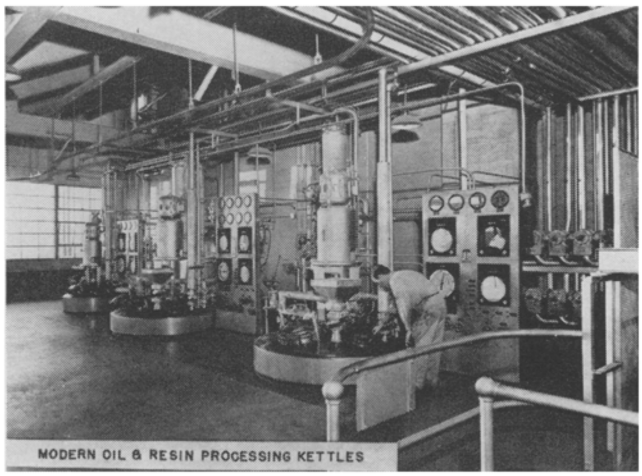

FIG. 1.

as provided by steam jet ejectors. An inert gas sparge of nitrogen and carbon dioxide is used in conjunction with the vacuum, and vigorous agitation is supplied by a direct drive turbine type agitator. Instrumentation of this equipment was very helpful in the study inasmuch as an automatic temperature control of ± 2°F. was obtained during each of these cooks. Indirect natural gas fires are used as the heat source. Rapid cooling of the processed oil is obtained by use of internal stainless steel coils employing water as the cooling medium.

The data obtained from the various runs is presented in graphical form. Viscosity is chosen as the common denominator, and in all cases zero time is taken as the time at which polymerization temperature is reached. It should be mentioned that the acid number was easily maintained at a rather low level, between 5 and 7, during all the cooks, hence a comparison of the acid numbers of the various oils was considered to be of no significance.

In considering the effect of temperature on the rate of polymerization (Fig. 2), it is found that safflower oil behaves in much the same manner as other fatty oils, possessing an appreciable degree of unsaturation.

[1] Presented at the 24th Annual Fall Meeting, American Oil Chemists' Society, San Francisco, Calif., Sept. 26-29, 1950.

TABLE I

	Safflower		Linseed		Soybean	
	Initial	Final	Initial	Final	Initial	Final
Viscosity						
(Poises)...........	0.4	55	0.4	56	0.4	40
(Gardner)........	A-	Z_3-Z_4	A-	Z_3-Z_4	A-	Z_2-Z_3
Color[a]..................	10	4	7-8	6-7	6	7-8
Acid value...........	0.41	6.5	0.50	6.25	0.52	3.5
Iodine number.....	142	99.5	175	113	135.5	85
Refractive index...	1.474	1.484	1.478	1.489	1.4742-1.4763[b]	....

[a] Gardner, 1933.
[b] Jamieson, F. G., "Vegetable Fats and Oils," p. 305, New York, Reinhold, 1943.

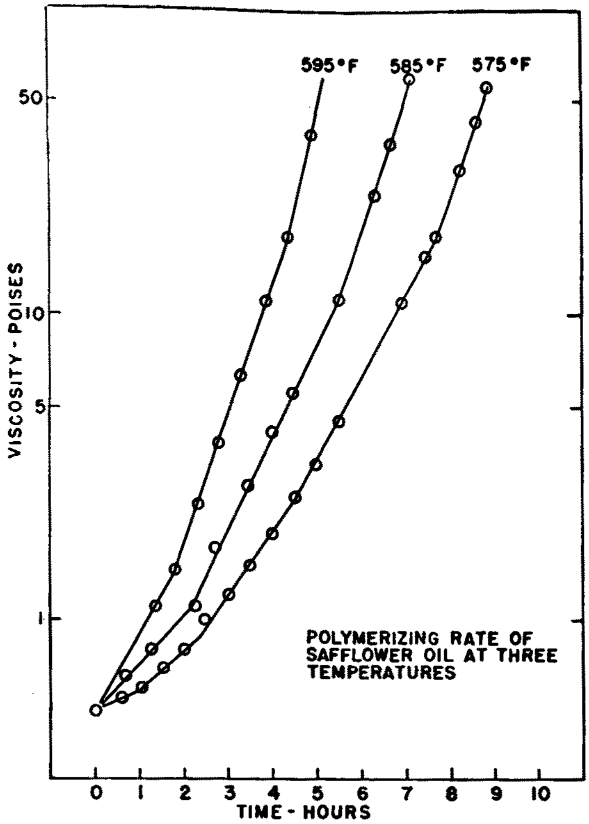

FIG. 2.

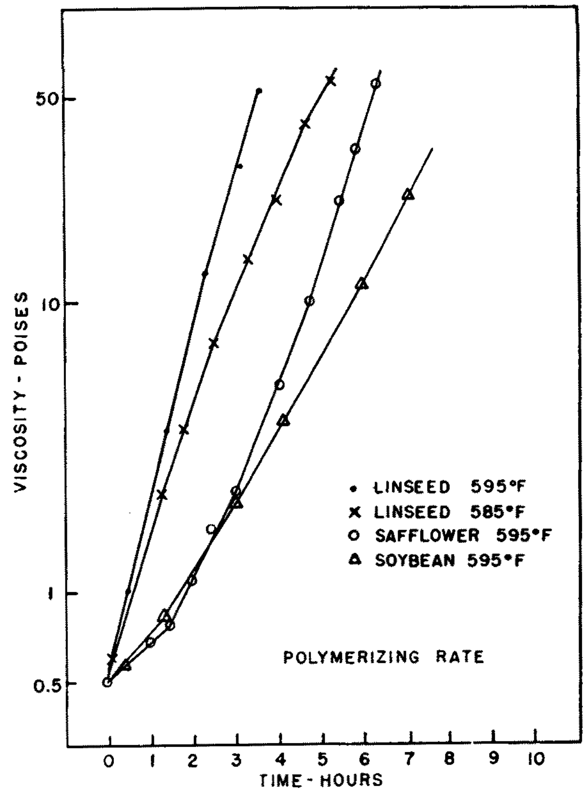

FIG. 3.

An increase of about 20°-25°F. in polymerizing temperature will result in a doubling of the average bodying rate (3). Close examination of the rate curves shows that the average bodying rate is not representative of the instantaneous rate at any given point, and it can be seen that the log viscosity-time curves for each of the three temperatures show definite discontinuities. These discontinuities are particularly apparent in both the 585°F. and 595°F. curves but are somewhat diffuse in the 575°F. curve. The curves are made up of three distinct linear segments. Although an explanation of this phenomenon is beyond the scope of this paper, it is interesting to note that discontinuities of a similar nature have been observed in work with other oils (4).

At this point we should like to mention that the effect of the processing equipment and procedure is extremely important in any study of this nature (5). The bodying rate and even the characteristics of the products are quite different when the processing is done in open kettle equipment rather than a closed vessel. Likewise the use of inert gas and/or vacuum has very definite effects. The batch yield is also affected to some degree by the type of equipment used and the processing procedure as well as the polymerization temperature.

A direct comparison of the polymerizing rate of safflower oil with that of linseed and soybean oil is made (Fig. 3). As one might expect from the iodine values of these oils, safflower bodies at a rate intermediate between linseed and soya. Again, however, the matter of average bodying rate versus instantaneous body rate becomes of interest. In the initial stages, before a viscosity of 1 poise is attained, safflower is much slower than linseed and is even a little slower than soya. In the case of soya this is contrary to what one would expect from the iodine values, but it is not too surprising when the component fatty acids of these two oils are considered (2, 6). In the intermediate stage safflower becomes considerably faster than soya but is still somewhat slower than linseed at the same temperature. It is very interesting

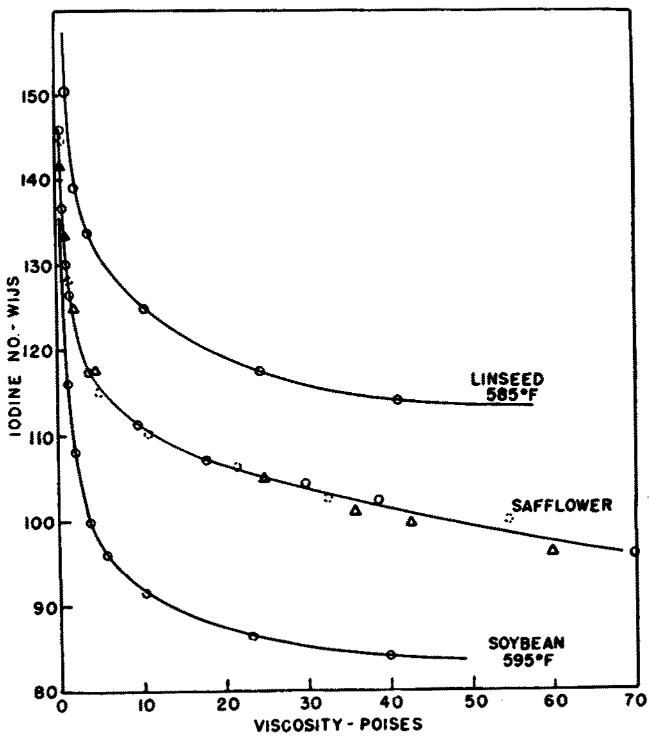

FIG. 4.

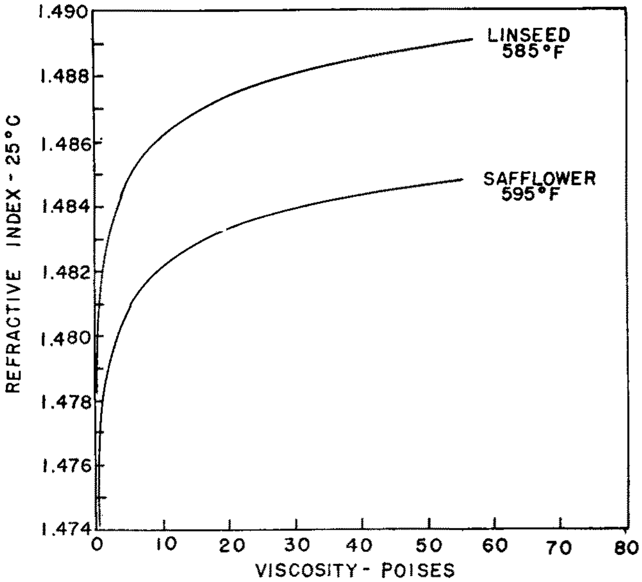

FIG. 5.

to note that in the viscosity range of 10 to 50 poises the polymerization rate of safflower closely approaches that of linseed. This rate continues until a viscosity of at least 80 poises is attained. Polymerization studies beyond 80 poises (Z_4-Z_5) should be of considerable interest. Thus it is evident that with the aid of a 10° increase in polymerization temperature, safflower oil may be bodied to a viscosity of about 50 poises (Z_4-Z_5) in approximately the same time as linseed and hence the same average rate.

The iodine value versus viscosity curves for the oils are shown in Figure 4. The curves are quite similar in shape except that in the range of 20-60 poises the iodine value of safflower oil drops at a faster rate than either linseed or soya. It should be noted that the curve for safflower is a composite curve and includes data from cooks at three temperatures. The 595°F. data is indicated by a circle, the 585°F. by a dotted circle, and the 575°F. by a triangle. The plotted points indicate that the composite curve is a good mean curve for all three temperatures. The refractive index versus viscosity curves (Fig. 5) are again about what one would expect.

One of the outstanding properties of safflower oil is its ability to bleach under heat treatment. The final constants of the oils given in Table I show this quite clearly. It might be well to mention here that the bodied safflower dries at a rate equal to or slightly better than bodied linseed but under certain conditions retains a slight degree of "after-tack" for a longer period of time.

Summary

It can be stated that the polymerization rate of safflower oil is sufficiently rapid to warrant its use on a commercial scale. Furthermore, with the proper choice of polymerization temperature, safflower can be bodied at the same rate as linseed. The increasing rate at which safflower bodies in the high viscosity ranges invites further investigation. In these higher viscosity ranges the iodine value continues to drop whereas in the same range the iodine numbers of other oils show a tendency to approach an asymptotic value.

Safflower heat bleaches considerably better than linseed and is also equal to or better than soya in this respect.

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The Effect of Screw-Press and Hydraulic-Press Processing Conditions on Pigment Glands in Cottonseed[1,2]

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WHEN cottonseed is processed by hydraulic-press procedures, many of the pigment glands are ruptured by the action of heat, moisture, and mechanical forces, and gossypol and related pigments escape from the ruptured glands. These liberated pigments react with the surrounding tissues to form "bound" gossypol which is considered to be physiologically inactive when ingested by farm animals (3, 5, 8, 13, 14). Although the by-product meal therefore contains a much smaller amount of unbound or free gossypol than the original kernels (5, 8, 14), the content is often too high to permit unrestricted feeding to non-ruminants, such as swine and poultry.

The effect of moisture and heat on pigment glands was determined by Boatner and her coworkers (4), who conducted laboratory tests in which cottonseed samples containing 7.6% and 41% moisture were heated at 241°F. for varying periods of time. In the material containing 7.6% moisture nearly all of the glands remained intact except after long exposure to heat whereas some of the glands in the moistened seed were ruptured even before heating and most of the remainder were ruptured by cooking. Likewise Williams *et al.* (12) noted that dry-cooked cottonseed meats contained very few ruptured glands whereas about 60% of the pigment glands were ruptured in meats which had been cooked with 20% of added

[1] Report of a study carried on under the Research and Marketing Act of 1946.

[2] Presented at the 42nd Annual Meeting of the American Oil Chemists' Society, May 3, 1951, New Orleans, La.

[3] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.