TABLE I

Weight Ratios of Reactants in the Epon 828/G-62/Phthalic Anhydride Series

Wt. % G-62	Pts. Epon 828 [a]	Pts. G-62 [b]	Pts. PA [c] for Epon 828	Pts. PA [d] for G-62
5	168.15	13.5	105.45	7.4
10	159.30	27.0	99.90	14.8
25	132.75	67.5	83.25	37.0
35	115.05	94.5	72.15	51.8
50	88.50	135.0	55.50	74.0
75	44.25	202.5	27.75	111.0
90	17.70	243.0	11.10	133.2

[a] Epoxide equivalent = 177.
[b] Epoxide equivalent = 270.
[c] Three-fourths equivalent = 111.
[d] One equivalent = 148.

proportions in parts by weight of the reactants for the epoxidized soybean oil series. When the phthalic anhydride was melted, the tubes were removed from the bath and inverted several times to insure good mixing. To each tube of the third series was added 0.5% of benzyldimethylamine, based on the total weight of the epoxides and curing agent, and mixing was again accomplished by inverting the tubes. All were returned to the oil bath and observed periodically for gelation.

When cured with phthalic anhydride, the 100% Epon 828 gelled in slightly more than two hours. The mixtures containing the amine gelled within four minutes. This rapid cross-linking caused severe internal stresses which resulted in fissures in the specimens. The epoxidized lard oil series required about three hours for gelation while the epoxidized soybean oil mixtures (without amine) gelled in varying times, which decreased as the concentration of diluent increased. At the 75% level the gel time had dropped to about one hour. All the specimens were kept in the oil bath for three hours to minimize cracking and then were transferred to a 150°C. air oven for a total cure of 20 hrs. When cool, the glass tubes were carefully shattered from the hard, transparent resins, and the latter were prepared for the physical measurements (7).

Summary and Conclusion

Three series of resins were made by curing mixtures of a diglycidyl ether and epoxidized, natural glycerides (lard oil and soybean oil) with phthalic anhydride. One property of the uncured system that was affected was the gelation time, a measure of the working pot life. All members of the epoxidized lard oil series took three hours to gel. The time of gelation of the epoxidized soybean oil series varied inversely with the concentration of diluent, and all members of the epoxidized soybean oil series containing tertiary amine gelled in four minutes.

Some physical properties of the resins were measured. The heat distortion temperature was a linear function of the percentage of epoxidized oil in each series. Up to 20% level both epoxidized glycerides had the same HDTs, but at higher concentrations the HDTs for the epoxidized lard oil resins decreased more rapidly. The blends containing a tertiary amine had HDTs constantly higher by 25 degrees than corresponding blends without amine.

The tensile strengths of the resins from each series decreased nonlinearly at the same rate up to a concentration of 20% of epoxidized glycerides. At higher concentrations the tensile strengths of the epoxidized lard oil series dropped the most and the amine-containing systems the least. Epoxidized lard and soybean oils appear promising as modifiers for diglycidyl ether resins up to a 20% level.

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Under discussion are investigations concerning a possible method of determining residual hexane present in solvent-extracted meal, using a modified Pensky-Martens closed-cup flash-point testing apparatus.

The standard apparatus and stirring motor were used. The major modification was to add two four-bladed propellers to the stirring shaft instead of the conventional single two-bladed propeller. One propeller was mounted on the bottom of the shaft and one about midway up. The blades of each propeller were turned so that they did not coincide or turn in the same plane vertically with each other. This imparted a twisting motion in the middle and upper portions of the sample as well as a complete movement on the bottom. The bottom propeller was adjusted so as to scrape the flat, round bottom of the sample cup and to come as close to the sides as movement would permit without binding. The upper propeller is of the same pitch and diameter as the bottom one, or one and three-fourths inches.

One other modification became necessary because of the change in propeller arrangement. The standard A.S.T.M. flash-point thermometers with 57 mm. or 2¼-in. immersion and with brass ferrules could not be used because of the interference from the upper propeller. A standard laboratory thermometer reading from 30° to 300°F. was used by equipping it with a tight-fitting cork, which was then mounted in the usual aperture on the head of the flash tester. Temperature checks with the thermometer thus placed and with the thermometer lowered to the bottom of the cup, with the meal sample in place, agreed so closely as to offer no objections to this method of mounting.

Sample Preparation

Samples of both a finely ground meal and a coarsely ground meal were prepared. The finely ground meal was chosen to represent average meals as ground in a laboratory Bauer mill. The coarsely ground meal was taken directly from oil mill production and was considered representative of the type of grinding encountered in meal as produced, stored, and/or shipped.

The fine meal was known to be solvent-free. It is the current laboratory check-meal and is used for quality control. It has been in use for 18 months with no variation in moisture content outside acceptable limits of tolerance. The coarse meal from the oil mill was first desolventized completely by evaporation over a steam bath for 4 hrs. The meal was spread very thinly over a wide area to insure maximum exposure to and penetration of heat. The moisture content of the coarse meal was then adjusted to its original basis; *i.e.*, 10%.

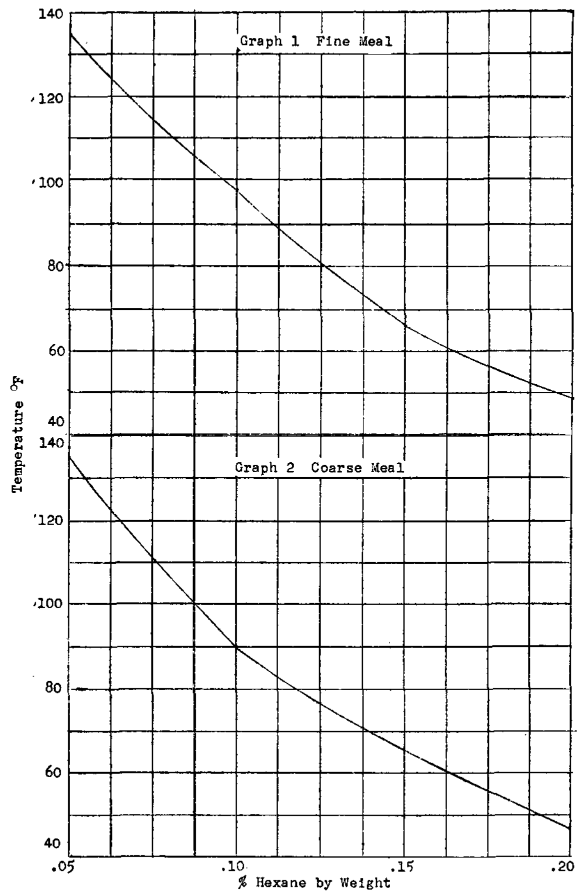
Percentages of hexane by weight were added to a series of each of the types of meal. Preliminary investigations had shown that percentages of 1.0, .5, and .25% were too high to yield anything but constant flashes and even fire regardless of temperature. Therefore concentrations of 0.025, 0.05, 0.1, and 0.2% hexane were chosen.

The method of addition was as follows. Small glass bottles with tight-fitting screw caps and good gaskets were tared. Hexane was added by dropper to the bottom of the bottle. Immediately meal was added, and the bottle was completely filled. In all cases there were at least 100 g. of total meal content in each bottle. The hexane was allowed to permeate the meal by natural diffusion at room temperature with the lids on the bottles tightly closed. After 1 hr. of standing at room temperature all samples were placed in the refrigerator, along with the sample cups and the thermometer. Samples were run in the inverse order of their hexane content to prevent the possibility of the flash machine not being completely cooled down to the sample temperature between runs as the high percentage hexane samples will flash at a lower temperature than the lower percentage samples. Duplicates were run on every sample. The sample weight used was 40 g. as this corresponds to the line on the inside of the cup used for measuring oil (60 ml.). All samples were kept in the refrigerator (40°F.) even between duplicate runs on the same sample.

For data see attached graphs. Averages of all 14 runs and their duplicates are plotted as temperature *versus* percentage of hexane. Individual runs were not plotted but were usually so close together that they would have been hard to read on a graph. One graph presents the picture for fine meal, one for coarse meal, and one for oil and hexane mixtures; the latter is for comparison.

Discussion

It was found that the conventional Pensky-Martens flash-point head and stirring motor were usable with no difficulties. No investigations were made with any other rate of stirring than the customary 2 rps. or 120 r.p.m. It was found however that the heating had to be turned much higher than for an oil sample in order to insure a uniform heat rise, or one of about 10 degrees per minute. The heat characteristics or enthalpy of meal is apparently much higher than that for oil, and the sensible heat is much greater.



Difficulty with all samples was encountered when temperatures of around 180° to 220°F. were reached. Moisture vapor became a real problem. Meals contain anywhere from 6 to 15% moisture, which is very much higher than that found in oils. The moisture vapor continually snuffs out the dip and pilot flames at these temperatures. Samples in all cases were carried to 260°F., and most were carried to 300°F., or until charring became so bad as to cause smoking. At this temperature the fine meals stuck together to form a core the size and shape of the containing cup and were stuck to the propellers. The coarse meals did not stick in any manner.

Close agreement between duplicates was found if proper caution was exercised. It was found that if duplicates were run within a few hours of each other on the same day, no noticeable drop in hexane content was found, provided the samples were kept refrigerated. However, if allowed to stand over-night even in the refrigerator and with lids screwed tightly, duplicates would not check closely even after inverting the bottles frequently to permit the hexane in the air above the meal to go back into the meal or spaces in the meal. Therefore samples were prepared fresh daily.

As can be seen from the graphs, the curves are rather flat as compared to the oil curve on an equivocal basis. The temperature spread is much less for meal than that for oil with corresponding percentages of hexane added, and the beginning and upper temperatures are both much lower. The lowest temperature found was 47°F., and the highest was 135°F. All of these temperatures are below the troublesome moisture vapor temperatures. No flashes were ever encountered in the percentage range chosen, in either the moisture vapor range or above it. With the low concentration of hexane (0.05%) the flash consisted of a single flame at the temperature quoted (135°F.). The higher the concentrations, the more often flashes could be observed until, during the 0.2% concentrations, flashes occurred every time the dip flame was lowered, or every 2 degrees from the beginning temperature of 47–49° to 140°F. "Pops" or minor explosions were common at this concentration, snuffing out the dip and pilot flames. No flashes were ever found in either type of meal for the hexane concentration of 0.025%.

Summary

A method of determining the residual hexane present in solvent-extracted meals has been investigated, using a modified Pensky-Martens closed-cup flash-point testing apparatus. The method is simple and requires little time. Elaborate and tedious precautions are not necessary. Good resolution and duplicatability were observed. The range for duplicates was from 0 to 10 degrees, from high concentrations to low concentrations.

The method has severe limitations however. Sample preparation or collection must be done carefully, preferably by trained personnel, lest this method measure only the hexane content of the sample as received and not relate to the amount of hexane present in the meal at the time of production or even at the time of sampling.

The range of detection is very limited, *i.e.*, from about .05% to .2%. Above these figures the method is not applicable or even feasible unless the entire machine can be constantly refrigerated at a very low temperature. Below these figures the flash points are either too elusive or nonexistent.

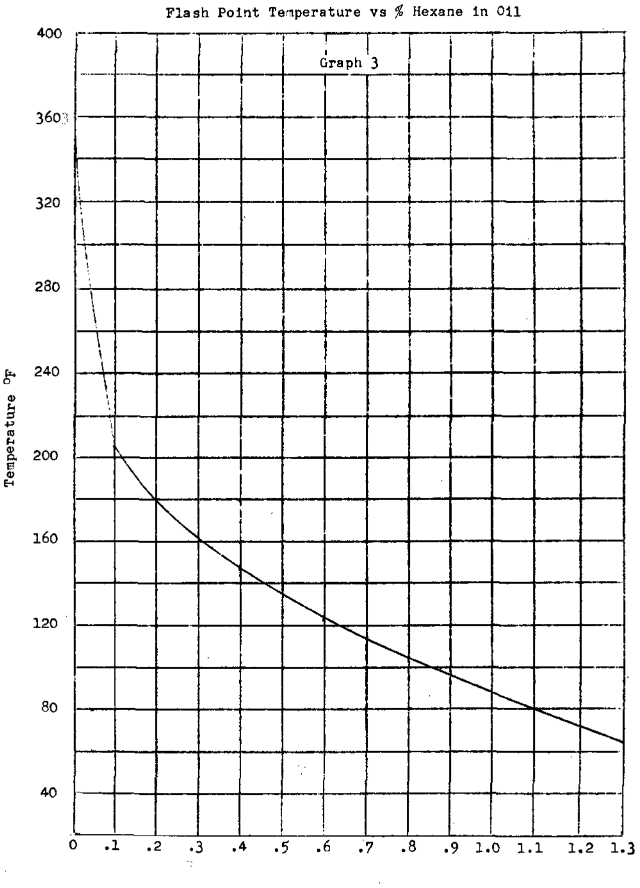
It is realized that the space above the meal in the cup is a confined space with little or no ventilation. Concentrations of air and hexane that are explosive are easily reached by the application of heat. The method therefore may have merit in that it may prove as a guide to upper and lower explosive limits of solvent-extracted meals in confined spaces such as boxcars, bins, or other types of bulk storage where ventilation is inadequate or nonexistent.

Two types of meal were chosen for several reasons. One was to see if particle size *per se* had any influence on the release or holding of hexane. Apparently very little difference occurs in this situation, or at least it was not discovered by this method. As can be seen by the figures, the fine and coarse meals flashed at close to the same temperatures for their corresponding percentage of hexane. No difference was noted in the amount of heat necessary or in the time consumed to run the test. Another reason for using the two meals was to serve as a basis of comparison in addition to comparing the meals with oil (Graph 3). Suffice it to say that under ordinary circumstances only the coarse or "mill run" meal would be tested. The grinding operation as performed in the laboratory would defeat the purpose of the test because heat from the mill plates and friction between particles would dispel some, if not all, of the hexane present. The open-type mixing of meal on paper after grinding would serve also to reduce the hexane present. The very effect desired in grinding, *i.e.*, reduction of particle size, also defeats our purpose when searching for residual hexane as reduced particle size also reduces the interstices and permits the hexane to escape faster because of increased surface contact. If this occurs and the air immediately surrounding the meal is not confined and limited, then much of the hexane is lost to atmosphere.

Moisture vapor is a serious problem in running the test. Any attempt to dry the sample before running would also defeat the purpose as the hexane would go out with the moisture, or at least this is true so far as is known. Perhaps some method analogous to the one used to remove water from oil could be employed though we have a different kind of problem in this case. We are dealing with a solid or solid-liquid (or vapor) mixture instead of a liquid-liquid solution.

As an afterthought it was decided to try adding hexane in miscella form to determine whether oil has any "holding power" on hexane. A 10% miscella was prepared, *i.e.*, 10% hexane and 90% crude cottonseed oil. By adding .25, .5, 1.0, and 2.0% by weight of this miscella to solvent-free meal samples, samples were obtained which contained .025, .05, .10, and .20% pure hexane, respectively. Mixing was somewhat more of a problem than it was when adding only hexane without oil. Three methods were tried.

First, the meal and miscella were mixed with a motor-drive propeller in a small jar fitted with a rubber-sealed hole in the lid through which the propeller shaft passed. The whole jar was kept cold in an



ice bath while mixing. Mixing time was 10 min. The results were not good, and duplicates did not agree. It is suspected that the jar used was too large and that too much air space existed above the meal sample and that hexane vapors were lost in transfer and also leaked out around the seal for it is rather difficult to form a vapor-tight seal around a moving shaft.

A second method of mixing was by natural diffusion. The miscella was added in small amounts throughout the entire meal sample at the time of weighing. The finished sample was placed in a jar with the sample completely filling the jar. The sample was allowed to stand at room temperature for one hour, then refrigerated for two hours. The results were better than the first method of mixing but were not considered reliable as duplicates did not agree more closely than 24°F. at the .1% hexane level.

A third method of mixing was tried, using a combination of the other two methods described. A sample of meal was weighed out. Miscella was added continuously during weighing so that miscella was rather thoroughly distributed throughout the sample. The sample was then placed in a jar just large enough to contain the entire sample. Mixing was accomplished by stirring, using the apparatus described in Method 1. Much better results were obtained by using this method. In one case duplicates agreed exactly, *i.e.,* 120°F. each at the 0.1% level of hexane.

In general, it was found that by using hexane in the form of miscella instead of "raw" that the flash points were from 20° to 30°F. higher for any given percentage hexane in the ranges selected. Also the same thing held true for miscella as for hexane in the matter of attenuation because of time. Samples kept any length of time, such as over-night, in a refrigerator flashed at higher temperatures than when run immediately after mixing and cooling. In the lower concentrations of hexane it was found that no flashes resulted after 24 hrs. where flashes had been found previously or when the samples were fresh.

In conclusion, it is thought that the flash-point tester has some merit but likely is not the ultimate answer to this problem. A great deal more work should be forthcoming on this and other methods in order to assure an accurate and reliable test for this pressing problem.

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The Determination of the Neutral Oil Content of Crude Vegetable Oils

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THE VARIOUS ATTEMPTS to devise methods for determining the refining loss of crude vegetable oils have resulted in three generally recognized methods: acetone-insoluble, Wesson, and chromatographic. The acetone-insoluble and the Wesson methods are not only time-consuming and elaborate but require considerable skill. Neither the Wesson method nor the A.O.C.S. cup method (3) give the actual percentage of crude oil. The chromatographic method, which is receiving increasing attention, uses a very flammable solvent, ether, which makes it undesirable, particularly for routine use.

The current method was based on the silicic acid column chromatographic method (1). Instead of using the usual column, the determinations were carried out in Erlenmeyer flasks. The apparatus used was 125-ml. Erlenmeyer flasks, sintered glass funnels, and a vacuum oven. The reagents were reagent-grade chloroform and reagent-grade powdered silicic acid. The soybean oil was a crude expeller-produced oil with a free fatty acid content of 0.6%.

Five grams of soybean oil were shaken for 10 min. in a flask with 50 ml. of chloroform and varying amounts of silicic acid and were filtered under vacuum. The silicic acid on the filter was washed with varying amounts of chloroform. The neutral fat content was also determined by the chromatographic method of Linteris and Handschumaker (2). The results are shown in Table I. Very good agreement with the results from the chromatographic method was obtained when the silicic acid was washed with a minimum of 300 ml. of chloroform.

TABLE I

Amounts of Neutral Oil Recovered from 2-g. Samples of Soybean Oil by Different Volumes of Wash Chloroform

Silicic acid in grams	25	50	100
Wash chloroform in ml.	Neutral oil in percentages		
100	88.0	87.8	87.5
150	88.8	89.0	88.7
200	89.6	89.5	89.0
250	92.6	92.5	92.4
300	93.1	93.0	92.9
500	93.1	93.1	93.0

Recovered by chromatographic method, 93.1%.

To determine if satisfactory results could be obtained with less chloroform, 2-g. samples were run with 25 g. of silicic acid and 50 ml. of chloroform. Results, using 250 ml. of wash chloroform (Table II), checked with those using 300 ml. of chloroform with the 5-g. oil samples.

Neutral oil was determined by this method on samples of corn oil and cottonseed oil. The corn oil was crude, produced from corn germs processed by prepressing, followed by solvent extraction, and had a free fatty acid content of 4.3%. The cottonseed oil was a crude expeller-produced oil with a free fatty acid content of 1.7%. Results are shown in Table III.

As the result of this work the following method for