Henkel & Cie G. m. b. H.: Fr. 794,422.
K. Keller & E. Gofferjé: Ger. 622,296 Cl. 12o.
J. O. Peirce: U. S. 2,042,410.
Rutgerswerke A.-G.: Fr. 787,546.
E. Segessmann: U. S. 2,054.140.
Standard Oil Development Co.: U. S. 2,049,055; 2,059,838; Brit. 449,169; 446,314.

Patents on sulfuric acid derivatives of compounds containing nitrogen, *e.g.*, amines, imides, amides, etc., intended for detergent use:

W. E. Billinghame: Brit. 443,719.
Böhme Fettchemie G. m. b. H.: Ger. 622,640 Cl. 12s; 627,055 Cl. 12s; 628,828 12p.
I. G. Farbenindustrie A.-G.: Ger. 623,226 Cl. 8o; Fr. 789.522: Ger. 635,241 Cl. 8o; Brit. 446,269; Fr. 787,819.
B. R. Harris: U. S. 2,052,027.
Henkel et Cie G. m. b. H.: Brit. 436,862; 442,135; 443,486; Fr. 789,578.
Imperial Chemical Industries, Ltd.: Brit. 435,039; 443,902; Fr. 794,578; 797;631; 786,625.
F. Pospiech: U. S. 2,055,588.
Soc. pour l'ind Chem. à Bâle: Brit. 449,043; Fr. 785,475; 799,220.
E. Waldmann & A. Chwala: Brit. 434,358.
J. Worslup: Brit. 450,672.

Patents on phosphoric acid derivatives of organic compounds intended for detergent use:

Böhme Fettchemie G. m. b. H.: Ger. 619,019 Cl. 12o.
B. R. Harris: U. S. 2,052.029; 2,026,785.
H. Bertsch & G. Rauchalles: U. S. 2,049.758.

Patents on nitrogen containing detergent; differing from those reported above under sulfuric acid derivatives of the compounds in that sulfonation was not claimed:

Deutsche Hydrierwerke A.-G.: Brit. 435,290; 443,265.
I. G. Farbenindustrie A.-G.: Brit. 438,793; 443,632; 446,416; 446,912; 449,081; Fr. 789.004; 795,662; 799,093.
Gesellschaft für Chemische Industrie; Brit. 449.209.
B. R. Harris: U. S. 2,023,075.
Henkel & Cie G. m. b. H.: Brit. 446,737.
H. Hunsdiecker & E. Vogt: U. S. 2,051.947.
F. W. Johnson: U. S. 2,040,997.
F. Munz and O. Bayer: U. S. 2.043,329.
Röhm & Haas Co.: U. S. 2,036,916; 2,045.517.
Soc. pour l'ind Chim. à Bâle: U. S. 2,043,164; Brit. 449,209; 449,661; Fr. 786,911; 796,192.

Patents on detergents from coal and mineral oil products differing from those previously reported in that none of the sulfuric acid derivitives are listed here:

A. Th. Böhme Chemische Fabrik: Ger. 628,062 Cl. 8k.
H. A. Bruson: U. S. 2,036,916.
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H. T. Ferrell et al.: U. S. 2,056,913.
H. Franzen: Ger. 627,808 Cl. 23e.
R. Heuter: U. S. 2,050,969.
J. Robinson: U. S. 2,040,673.
W. Schrauth: U. S. 2,036,438.

Miscellaneous detergent patents:

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I. G. Farbenindustrie A.-G.: Fr. 800,079; 787,785; Ger. 623,404 Cl. 12s.
B. R. Harris: U. S. 2,025,984.
Henkel & Cie G. m. b. H.: Brit. 446,498.
Imperial Chemical Industries, Ltd.: Fr. 785.800.

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R. C. NEWTON
H. A. MATTILL
GEO. S. JAMIESON
G. R. GREENBANK

CHANGES IN THE PHOSPHATIDE CONTENT OF CRUDE SOYBEAN OIL DURING STORAGE*

By GEORGE E. HALLIDAY

Department of Agricultural Chemistry, Purdue University Agricultural Experiment Station, Lafayette, Indiana

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WHEN domestic crude soybean oil began to appear on the market in this country much of it was cloudy and inferior to the crude soybean oil imported from the Orient[2, 6]. Three explanations have been offered to account for this difference between the Oriental and the domestic product. Junker[5] stated that modern methods of oil extraction removed a large amount of other materials along with the fat while the crude Manchurian press method removed only the oil. Pickard[6] and Eastman[2] attributed the poor quality of the domestic oil to failure of the producers to master the art of filtering the oil. Gardner[3] compared several domestic and imported oils and reported that some samples of domestic oil showed a considerable amount of foots, indicating that the oil had not been allowed to settle long enough.

Smith and Kraybill[7] showed that the material responsible for the "break" in soybean oil consists of crude phosphatides. They removed these materials by two different methods and obtained "non-break" soybean oil. When the product removed was added to this "non-break" soybean oil the soybean oil was again converted into "break" oil. Jamieson and McKinney[4] found that the precipitate that separated from expressed crude soybean oils on standing consisted chiefly of crude phosphatides.

An opportunity to study the changes in the phosphatide content of crude soybean oil during storage was presented in Lafayette, Indiana, on January 28, 1933. At that time fifteen carloads of soybean oil which had been produced at a local mill within a period of four months were held on track in the railroad yards. This mill was crushing principally Manchu and Dunfield soybeans. The oil was obtained by the use of Anderson expellers, filtered immediately through a filter-press, stored for not more than three days in the mill, and then loaded into tank cars. Some of the cars had been steamed out just before being loaded and probably contained more moisture than the others, but these cars could not be identified from the data available. Movement due to switching provided a small amount of agitation of the oil during the storage period.

Sampling. The tank cars of soybean oil were sampled through the trapdoor in the turret. The sampler used had a diameter of four inches and was fitted with a sleeve valve. In sampling the oil the valve was closed and the sampler placed in the car to the desired depth, the valve was opened and quickly closed again, and the sampler withdrawn. The oil in the sampler was mixed well and a two-ounce bottle filled from the mixed sample.

Three samples were taken from each car as follows: (1) the surface oil, (2) the middle layer of oil, and (3) the material on the bottom of the car. In some cases the material on the bottom was so thick that it would not run into the sampler and in these cases the sample was taken as deep in the car as the sampler would operate.

A description of these samples was obtained immediately and is included in Table 1. The samples were then carefully mixed and worked to a uniform consistency with a spatula. The total phosphorus contained in each sample was then determined in duplicate.

Determination of Total Phosphorus. Approximately five grams of the sample was placed in a weighed ten centimeter porcelain evaporating dish and the exact weight of the oil determined, ten

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*These data are from a thesis submitted by G. E. Halliday to the Faculty of the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Master of Science, August, 1934.

cc. of a saturated alcoholic solution of magnesium nitrate (95 per cent alcohol saturated with $Mg(NO_3)_2 \cdot 6H_2O$ crystals) was added, and the sample placed on the steam bath. A tough surface layer was formed by heating overnight. The dish was then placed on an electric hot plate and carefully heated until the sample charred; too rapid heating was avoided. The charred sample was then placed in a cool muffle furnace and heated to 600° C. for three hours or until completely oxidized. The evaporating dish was then cooled and the fluffy ash carefully moistened with water and then dissolved with concentrated hydrochloric acid. The solution was transferred to a 250 cc. beaker, evaporated to a small volume, filtered, and the filter washed free from chlorides with hot water. Filtrate and washings were collected in another 250 cc. beaker and the volume adjusted by evaporation. The phosphorus was determined in the total sample according to the volumetric method described in the Official and Tentative Methods of Analysis of the A.O.A.C.[1]

For convenience in expressing the results it was assumed that all of the phosphorus present in the samples was combined in a stearyloleyl lecithin having the formula $C_{44}H_{88}O_9NP$ and containing 3.85 per cent phosphorus. The data thus obtained are shown in Table 1.

Discussion. In Table 1 the cars are arranged according to the time of loading, the cars filled first being at the top of the table and those filled most recently being at the bottom. When considered according to the age of the oil these cars can be divided into three groups. The cars which have been standing more than seventy-five days consist of an upper layer of oil containing less phosphatides than the fresh oil normally contains, and a layer on the bottom of the car which contains much more phosphatide than a normal oil contains. The cars which have been standing for a period of twenty-five to seventy-five days show this same accumulation of the phosphatides in the lowest layer, but to a lesser extent; in most cases the solid material is just beginning to accumulate on the bottom of the car. The oils which have been standing less than twenty-five days are still fairly uniform in composition, resembling the fresh oil throughout. Comparison of the surface and middle oil shows that the upper half of the car is of uniform composition in every case.

The large differences in phosphatide content of the bottom layers of oils of about the same age cannot be accounted for satisfactorily due to lack of data. However, it has been shown that when moisture is mixed into the oil there is a separation of yellowish hydrated phosphatides.[7] It is probable that the cars containing a thick sludge having a high phosphatide content are those which contained some moisture when the oil was loaded and that this moisture has hydrated the phosphatides of the oil and produced a more rapid separation than would occur in ordinary settling.

TABLE 1

Car Number	Days in Storage	Per cent Lecithin in Top Oil	Per cent Lecithin in Middle Oil	Per cent Lecithin in Bottom Oil	Description of Bottom Oil* Amount of Precipitate	Description of Bottom Oil* Color
1**	112	0.72	0.65	5.65	Medium	Normal
2	104	0.77	0.83	20.17	Large	Very light
3	100	0.85	0.85	6.48	Medium	Dark
4	97	1.15	1.11	10.63	Small	Dark
5	93	1.07	1.05	13.80	Medium	Dark
6	89	1.18	1.14	22.35	Large	Light
7	73	1.08	1.04	6.55	Large	Normal
8	69	1.28	1.29	9.33	Medium	Light
9	66	1.45	1.45	5.36	Large	Light
10	64	1.41	1.41	7.28	Trace	Dark
11	46	1.25	1.24	3.92	Trace	Normal
12	29	1.14	1.16	4.37	Trace	Normal
13	16	1.40	1.34	1.60	None	Normal
14	6	1.37	1.32	1.45	None	Normal
15	3	1.27	1.34	3.08	Trace	Normal

*All of the Top Oil and Middle Oil was free of precipitate and of normal color.

**This car was first loaded 315 days before sampling and the oil has been refiltered four times, the last time 112 days before sampling.

SUMMARY

Fifteen carloads of crude soybean oil which had been in storage from three to 112 days were sampled at three levels and the total phosphorus content of each sample determined. The oil from the surface to the middle of the car had a uniform phosphatide content. The phosphatide content of the material on the bottom of the car increased with the increasing length of the storage period and this increase was accompanied by a decrease in the phosphatide content of the oil in the upper layers of the car.

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PROPOSED METHOD FOR COLD TEST ON REFINED OILS

Four ounce sample bottles which are perfectly dry are used in this test. If there is any doubt as to the dryness of the bottle, place it in an oven at 105° C. for one hour and cool in a desiccator. These precautions are necessary because a small amount of moisture will vitiate the test.

If the oil sample is received during cold weather and seems to have been chilled already, heat to 35°, and hold it 4 to 5 hours at about 25° C. (or preferably over night) to put the oil in proper condition for the test.

The sample must always be tested as received (except as modified in the preceding paragraph where the sample has been received in cold weather or has been chilled already).

However, if it is desired to determine whether a failure to pass the test is due to moisture in the oil, heat the oil to 105° C. and hold at this temperature until the last traces of moisture have been removed, then cool to 25° C. and hold overnight at this temperature before repeating the test.

Fill the bottle half full of the oil, insert a cork stopper tightly and cut off the end of the latter flush with the top of the bottle. Seal well with paraffin. Immerse in a container filled with cracked ice and just sufficient cold water to fill the container to the top of the