cial hexane can be calculated by means of the following equation:

$$S = S_{II} + \Delta S_{oil} \left(\frac{P}{100} \right) + \Delta S_{hex} \left(\frac{100\text{-}P}{100} \right)$$

where S_{II} is the value read from Table II by interpolation; ΔS_{oil} is the specific gravity of the given oil at any temperature minus that read from the table; and ΔS_{hex} is the specific gravity of the given hexane at any temperature minus that obtained from Table II.

It is apparent that if Table II is used for determining the concentration of a random rice bran oil-hexane miscella an accuracy of one percentage unit will be attained even if the value of $S - S_{II}$ is as large as ± 0.0018 at low oil concentrations and ± 0.0030 at high oil concentrations. If a commercial hexane having a specific gravity appreciably different from that in Table II is to be used extensively, it may be desirable to calculate corrections for all the values in the table and thus construct a new table which will be directly applicable with a correction only for an appreciable difference in the specific gravity of the random rice bran oil.

It was found that satisfactory agreement was obtained when Table II was applied to a hexane miscella of crude rice bran oil. This miscella, obtained from a pilot-plant rice bran extraction, had a specific gravity at 77°F. of 0.7042. Analysis by stripping off the solvent showed that it contained 11.84% by weight of oil having a specific gravity at 77°F. of 0.9165. The specific gravity of the original solvent at 77°F. was 0.6812.

The uncorrected specific gravity read from Table II for an 11.84% oil mixture is 0.7031, which is in satisfactory agreement with the experimental value, 0.7042, considering the accuracy attainable by means of commercial hydrometers. Conversely, if the experimental specific gravity, 0.7042, is applied to determine the concentration by use of the table, 12.42% is obtained instead of 11.84%.

Better agreement is obtained if correction is made for the fact that the specific gravities at 77°F. of the oil and the hexane used were 0.9165 and 0.6812, respectively, instead of 0.9163 and 0.6803, the corresponding values obtained from the table. Thus S_{II} in the above equation is 0.7031, ΔS_{oil} equals $+ 0.0002$, and ΔS_{hex} equals $+ 0.0009$, and the calculated specific gravity, S, equals 0.7039, which agrees within experimental accuracy with the value found. The experimental values were determined before the dissolved waxes had time to come out of solution.

Summary

Complete density-composition-temperature data have been obtained for binary systems of a refined rice bran oil with a commercial hexane. They have been presented in the form of a table which gives the specific gravities at 5% intervals of concentration and at 10 Fahrenheit-degree intervals of temperature and can readily be converted to other density units. These data can be used to determine the specific gravity, knowing the composition and the temperature, or, conversely, the composition, knowing the specific gravity and temperature, and should be useful in commercial processing and control. For high accuracy a small correction must be applied for random refined and crude rice bran oils and for different commercial hexanes.

REFERENCES

1. Magne, F. C., and Skau, E. L., Ind. Eng. Chem., 37, 1097-1101 (1945).
2. Magne, F. C., Hughes, E. J., and Skau, E. L., J. Am. Oil Chem. Soc., 27, 552-555 (1950).

Rice Bran Oil. VIII. Tank Settlings From Crude Rice Bran Oil as a Source of Wax[1,2]

EDWIN R. COUSINS, S. P. FORE, H. J. JANSSEN, and R. O. FEUGE, Southern Regional Research Laboratory,[3] New Orleans, Louisiana

IN the extraction of oil from rice bran a certain amount of wax is removed with the oil. The yield of wax varies with the temperature at which the extraction is made, the solvent used, source and history of the bran, and a number of other factors. Yields of 3-9%, 5.7%, and 6.4%, on a total lipid basis, have been reported (8, 9, 13). It is probable however that most of the crude rice bran oil presently produced in the United States contains only 1 or 2% of wax because no attempt is made to extract it with the oil.

In spite of the estimated yields of 1 or 2% several facts indicate the wax may become a regular article of commerce. Rice bran oil is being produced in the cars of crude oil per year, and at least two new extraction plants are scheduled to begin operation in the near future. Not only is a sizeable amount of crude wax already available with more becoming available, but it is at present regarded somewhat as a nuisance. The high-melting fraction of the wax is quite insoluble in the oil and settles out as a voluminous, oil-rich sludge which at present has little value.

Tank settlings domestically available, which are generally from crude oil extracted with commercial hexane, vary in composition and quality, as might be expected. Those from crude oil extracted from bran of good quality are usually tan to brown in color and possess the rather pleasant odor characteristic of crude rice bran oil. Their consistency varies from that of soft butter to that of a heavy, viscous liquid.

The solid and liquid portions of tank settlings can not readily be separated by filtration. Any filter fine enough to retain the solids clogs almost immediately on use. The addition of hexane to settlings permits

their filtration at a more rapid but still unsatisfactory rate. The addition of acetone to settlings produces a mixture which does filter readily. Furthermore the wax is only slightly soluble in the latter solvent (8). Isopropanol behaves somewhat like acetone as a solvent for settlings.

Samples of tank settlings examined in the laboratory consisted principally of oil and free fatty acids derived from the oil. The remaining portion contained in addition to the wax a sizeable proportion of phosphatides. Usually particles of meal, trash, and calcium carbonate (frequently used in the milling of rice) were present in minor amounts. Undoubtedly the settlings also contained some gums, resins, and degraded organic matter.

The object of the present work was to investigate methods of separating the wax from the other materials in tank settlings from crude rice bran oil by applying various purification procedures and to compare the yields and quality of the wax fractions separated by the different procedures. The wax fractions were not analyzed with the object of establishing the nature of their individual chemical components. Other workers (4, 6, 10, 11, 12, 15) have examined the composition of rice bran wax and have reported that the compounds present include myricyl alcohol, ceryl alcohol, myricyl cerotate, and other esters of myricyl alcohol, some unsaturated acids and alcohols containing about 26 carbon atoms, and phytosterols.

Tank Settlings Used as Starting Materials

Portions of a single, 400-pound batch of tank settlings were used as starting material for all except one of the wax purification experiments which will be described. This batch, identified as S-1, was obtained from a leading commercial processor of rice bran oil. Unless specifically stated otherwise, the term "tank settlings" hereafter will refer to sample S-1. The settlings were of a light brown color and possessed a good odor; they were considered to be a more or less normal product. The analyses described in Table I

TABLE I

Analysis of Tank Settlings and of an Acetone-Insoluble and an Acetone-Soluble Fraction

	Sample S-1	Acetone[a] insoluble fraction of S-1	Acetone[b] soluble fraction of S-1	Sample S-2
Iodine value	77.0	29.6	103.2	71.8
Free fatty acids, as oleic, %	21.6	10.7	24.1	6.5
Volatiles, hot plate method, %	4.1	3.3		6.5
Saponification value	166.7		181.8	179.8
Unsaponifiable, %	14.0	44.8	2.7	10.3
Phosphorus, %	0.44	0.79	0.13	1.64
Hexane soluble, %[c]	96.4			79.4

[a] Composite of several samples.
[b] Sample from a single fractionation run.
[c] Continuous extraction with hot hexane for 3 hours.

show that 96.4% of these settlings were soluble in hot hexane; therefore only a small amount of bran and dirt could have been present. The phosphorous content of the settlings was 0.44%, which would correspond to a phosphatide content of 11%, but probably some portion of this phosphorus was not present as phosphatides. The volatile component, which amounted to 4.1%, consisted partly of water. The iodine value of 77.0 for the tank settlings is appreciably below the value of approximately 100 for crude rice bran oil.

Tank settlings S-2, which were used in one purification experiment, were dark brown in color and possessed an odor similar to that of charred organic matter. Only 79.5% of these settlings could be dissolved in hot hexane. Much of the insoluble portion appeared to be bran, whose presence of course makes difficult the interpretation of the analyses. Probably settlings S-2 were representative of the lower grades obtainable commercially.

Before each portion of settlings was used, is was melted and filtered through a 60-mesh sieve to remove any coarse trash.

Methods of Analysis

There are no standard methods for analyzing waxes. The methods of the American Oil Chemists' Society (1) for analyzing fats and oils are suitable for some analyses involving waxes and were used in the present investigation to determine iodine value, free fatty acids, volatiles, softening point, and saponification value. In the latter determination isopropanol was substituted for the ethanol specified in the standard method.

Content of unsaponifiables was determined by the method of Murray and Schonfeld (5), which they found suitable for carnauba wax.

For the phosphorus determination the sample of wax was ashed with the aid of alcoholic magnesium nitrate and was then analyzed according to the method of Pons and Guthrie (7).

All melting points reported were obtained by the drop method (14), which consists essentially of solidifying a film of wax on the bulb of a thermometer, slowly heating the coated bulb in an air bath, and recording the temperature at which the wax melts and collects in a drop at the bottom of the bulb.

Hardness of the waxes was measured at room temperature, using the Shore durometer method described by Warth (14). On the durometer scale yellow U.S.P. beeswax has a hardness of about 45 and 90% palmitic acid has a hardness of about 50, both measured at 25° C.

Purification Procedures

Tank settlings were processed by five different procedures to obtain a hard, high-melting wax fraction. Two of the procedures involved treatment of the acetone-insoluble portion of the tank settlings. In one case the insoluble portion was hydrolyzed and then purified by fractionation from isopropanol; in the other, it was saponified and then purified by fractionation from isopropanol. A third procedure involved hydration of the tank settlings followed by fractionation of the oil phase from isopropanol. The other two procedures involved simple fractionation of tank settlings from solvents; in one case, diethyl ether and isopropanol, and in the other isopropanol only.

Hydrolysis and Saponification. Isolation of the acetone-insoluble fraction of the tank settlings was the common, initial step for the procedures involving hydrolysis and saponification. This step was performed as follows. One part of acetone was mixed with one part of tank settlings, and the mixture was filtered under vacuum. The mixing with acetone and filtration were repeated twice, using half of the original quantity of acetone each time. The acetone-insoluble or wax fraction then was air-dried for 48 hours.

Air-drying changed the acetone-insoluble fraction into a tan-coolred powder that was slightly tacky to the touch. In weight it was equal, on an average, to

TABLE II

Chemical and Physical Analysis of Refined Rice Bran
Wax and Carnauba Wax[a]

Sample	Yield [b]	Free fatty acids	Iodine value	Unsapon- ifiable	Saponi- fication value	Phos- phorus	Volatile matter	Melting point, drop method	Softening point	Color
	%	%		%		%	%	°C.	°C.	
A-6	13.7	2.7	13.0	57.5	104.4	0.01	0.66	75.8	75.3	Black
B-8	12.8	7.3	13.6	67.0	56.9	0.01	2.94	78.7	76.7	Dark Brown
C-7	8.3	5.5	17.7	56.0	79.9	0.15	0.62	78.9	77.0	Brown
D-8	9.1	2.7	11.1	56.0	77.9	0.08	0.41	79.9	79.0	Brown
E-13	11.6	2.1	16.3	57.2	84.6	0.11	0.38	78.7	76.7	Brown
F-13	3.4	2.7	19.4	55.1	80.4	0.18	0.61	75.3	74.3	Black
Carnauba		2.9	9.4	56.9	77.0	0.00	0.25	83.4	82.5	Tan

[a] All samples were non-tacky and possessed a Durometer Hardness of 100.
[b] Based on original weight of screened tank settlings.

23.8% of the tank settlings (S-1) used in its preparation. The third column in Table I lists the analysis of a composite of acetone-insoluble fractions obtained by treating 20 gallons of tank settlings in small portions while the fourth column lists the analysis of the acetone-soluble fraction from one of these portions after removal of the acetone. The latter fraction contained practically no solids at room temperature.

The acetone-insoluble fraction represented in Table I is a relatively impure wax containing about 20% of phosphatides. Some occluded oil and fatty acids probably are present because the wax is not dissolved in the acetone treatment. Particles of bran, inorganic matter, and certain gummy substances also are concentrated in this fraction.

In the purification procedure involving hydrolysis one part of the acetone-insoluble fraction was placed in a stainless steel fat-splitting kettle with one part of water, and the phosphatides were hydrolyzed under such mild conditions (1 hour at 177°C.) that the wax esters present probably were not affected. The hydrolyzed material was washed with water, dried, and fractionally crystallized from an isopropanol solution. Figure 1 shows the details of the procedure and the yield obtained.

Fraction A-2 was black in color, possibly owing to charring of some of the gummy material in the acetone-insolubles during the heat treatment. This fraction contained only 0.08% of phosphorus. Results of another hydrolysis of the acetone-insoluble fraction for 4 hours at 232°C. indicated that the phosphorus content could not be reduced further by increasing time and temperature. The residual phosphorus is not believed to be present in the form of phosphatide. Fraction A-4 consisted mainly of black-colored degraded material. Fraction A-6 was the end product or purified sample of hard rice bran wax. Its chemical and physical properties are recorded in Table II.

A slight variation of the process represented in Figure 1 was also investigated. Because soluble fraction A-3, as represented in Figure 1, actually consisted of a main liquid phase in which droplets of at least one other liquid phase of higher density were suspended, it was thought that a better grade of wax might be produced by decanting, while hot, the main isopropanol solution from the solid portion and heavier liquid phase. Such a decantation yielded an A-3 fraction containing 19.0% of the acetone insolubles used as starting material. The yield of the corresponding A-4 fraction was 49.3% while that for the corresponding
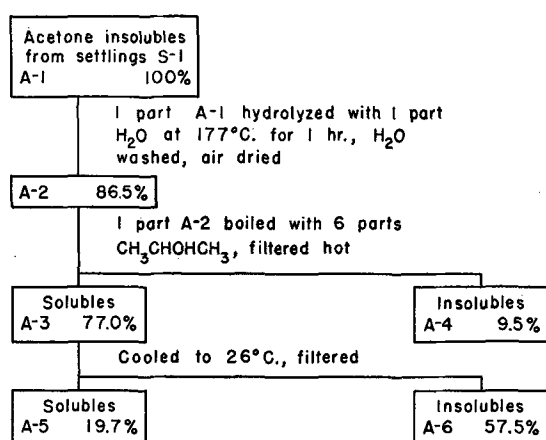
FIG. 1. Preparation of wax A-6 from acetone-insoluble portion of tank settlings S-1.

In this and the other flow sheets shown below, the sums of the various end fractions do not always equal 100% because of minor losses in moisture or material or minor gains caused by incomplete removal of solvent. Some of the yields shown for the intermediate fractions were calculated by difference.
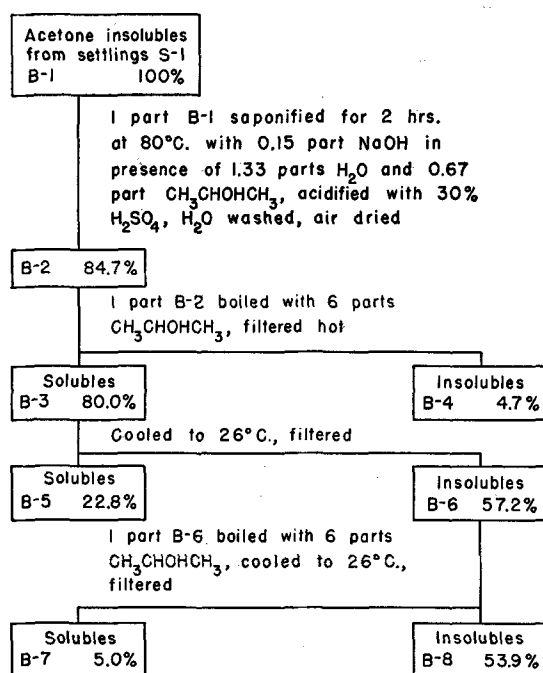
FIG. 2. Preparation of wax B-8 from acetone-insoluble portion of tank settlings S-1.

A-6 fraction, or final product, was 17.3%. The final product obtained by the decantation method was lighter in color than that obtained by filtration, but it also was somewhat softer in consistency.

For the purification procedure involving saponification of the acetone-insoluble fraction represented in Table I, the fraction was saponified, acidulated, washed with water, dried in air, and fractionated from isopropanol as depicted in Figure 2. The properties of the final fraction, B-8, are listed in Table II.

Hydration. The methods of hydrolysis and saponification just considered for the removal of phosphatides in the purification of wax involved their destruction. Phosphatides can be removed as such by making use of the fact that they hydrate rapidly in the presence of water to form an oil-insoluble mass which separates out of the oil phase. Figure 3 represents a
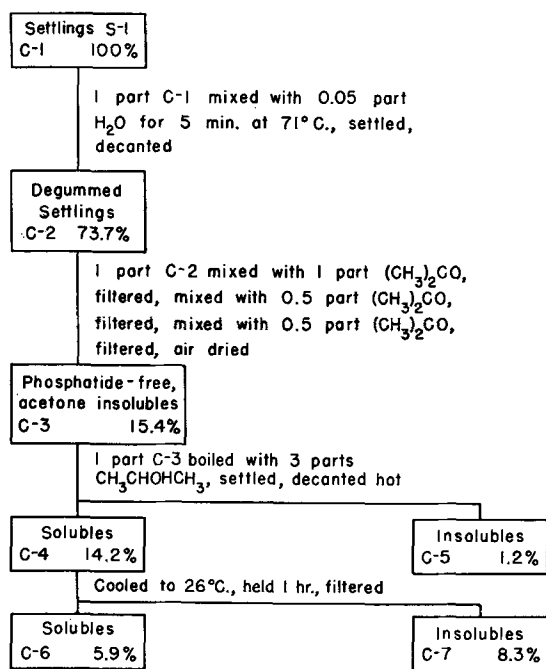

FIG. 3. Preparation of wax C-7.

simple procedure incorporating this fact and shows what yields were obtained with tank settlings S-1.

In the procedure shown in Figure 3 the small amount of water required for hydration was sprayed onto the settlings while they were being mixed rapidly after having been heated to 71°C. to melt the wax. The emulsion which formed broke readily when the mixing was discontinued and the temperature held at 71°C. Not only did the phosphatides settle out, but they also carried down insoluble impurities. Separation of the aqueous and oil phases by decantation was not entirely satisfactory. After the degumming step the settlings were fractionated using acetone and isopropanol to separate the oil and wax. Fraction C-7 is the end product or hard-wax fraction. Its properties are listed in Table II.

Solvents. The isolation of a hard wax from tank settlings was also accomplished entirely by fractionation from solvents. Figure 4 is a flow sheet for such a fractionation of tank settlings through the use of diethyl ether and isopropanol. The phosphatide and oil portions of the settlings were removed by dissolving

them in diethyl ether which did not dissolve the hard wax. Isopropanol was used further to purify the wax fraction to obtain the final product D-8, which is also listed in Table II.

In another procedure for separating wax from tank settlings only isopropanol was used. Figure 5 gives the details and the yield obtained. Table II lists the properties of the final wax fraction E-13.

The wax fraction F-13 listed in Table II is the fraction corresponding to E-13 when tank settlings S-2 were treated. For purposes of comparison the table also lists analyses made on a good grade of carnauba wax.

Bleaching of Wax

All of the samples of rice bran wax listed in Table II were practically black in color when liquid. Bleaching with approximately 10% of activated clay or carbon had little effect on this color. Bleaching with hydrogen peroxide was effective. A combination of hydrogen peroxide, chromium trioxide, and sulfuric acid (11) was found to be particularly effective and resulted in a practically white wax.

In a typical bleaching with hydrogen peroxide 1 part of sample B-8 was added to 4 parts of water and 0.5 part of 29% hydrogen peroxide, and the mixture was stirred for 2.5 hours at about 95°C. After the bleached wax was washed with water and dried, it had a Gardner color (10) of 18 in the liquid state and a bright tan color in the solid state. When the bleaching procedure was modified by the addition of 4.5 parts of 40% sulfuric acid to the bleaching mixture and an increase in the bleaching time to 3.5 hours, there was no improvement in the color of the bleached wax.

In a typical bleaching with chromium trioxide 1 part of sample C-7 was mixed with 4.5 parts of 40% sulfuric acid. While the mixture was at a temperature of 95°C., 0.5 part of chromium trioxide was added slowly and with constant stirring. Heating and stirring were continued for a period of 2.5 hours, and then the sample was washed successively with 40%
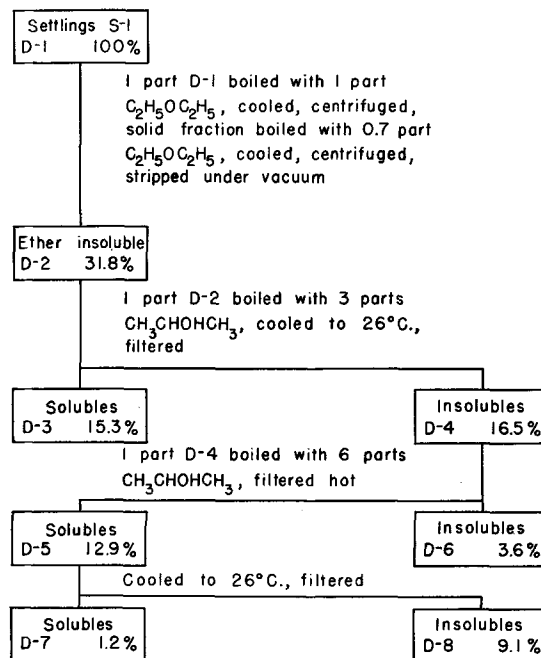

FIG. 4. Preparation of wax D-8.

```
┌─────────────────────┐
│ Settlings  S-I      │
│ E-I        100%     │
└─────────────────────┘
        │ I part E-I boiled with 3 parts
        │ CH₃CHOHCH₃, settled, decanted hot
  ┌─────┴──────────────────────────────────┐
┌───────────────────┐            ┌───────────────────┐
│ Solubles          │            │ Insolubles        │
│ E-2      86.4 %   │            │ E-3      13.6 %   │
└───────────────────┘            └───────────────────┘
        │ Cooled to 26°C., held I hr., filtered
  ┌─────┴──────────────────────────────────┐
┌───────────────────┐            ┌───────────────────┐
│ Solubles          │            │ Insolubles        │
│ E-4      67.8 %   │            │ E-5      18.6 %   │
└───────────────────┘            └───────────────────┘
        │ I part E-5 boiled with 3 parts
        │ CH₃CHOHCH₃, settled, decanted hot
  ┌─────┴──────────────────────────────────┐
┌───────────────────┐            ┌───────────────────┐
│ Solubles          │            │ Insolubles        │
│ E-6      18.1 %   │            │ E-7      0.5 %    │
└───────────────────┘            └───────────────────┘
        │ Cooled to 26°C., held I hr., filtered
  ┌─────┴──────────────────────────────────┐
┌───────────────────┐            ┌───────────────────┐
│ Solubles          │            │ Insolubles        │
│ E-8      4.2 %    │            │ E-9      13.9 %   │
└───────────────────┘            └───────────────────┘
        │ I part E-9 boiled with 3 parts
        │ CH₃CHOHCH₃, settled, decanted hot
  ┌─────┴──────────────────────────────────┐
┌───────────────────┐            ┌───────────────────┐
│ Solubles          │            │ Insolubles        │
│ E-10     12.0 %   │            │ E-II     1.9 %    │
└───────────────────┘            └───────────────────┘
        │ Cooled to 26°C., held I hr., filtered
  ┌─────┴──────────────────────────────────┐
┌───────────────────┐            ┌───────────────────┐
│ Solubles          │            │ Insolubles        │
│ E-12     0.4 %    │            │ E-13     11.6 %   │
└───────────────────┘            └───────────────────┘
```
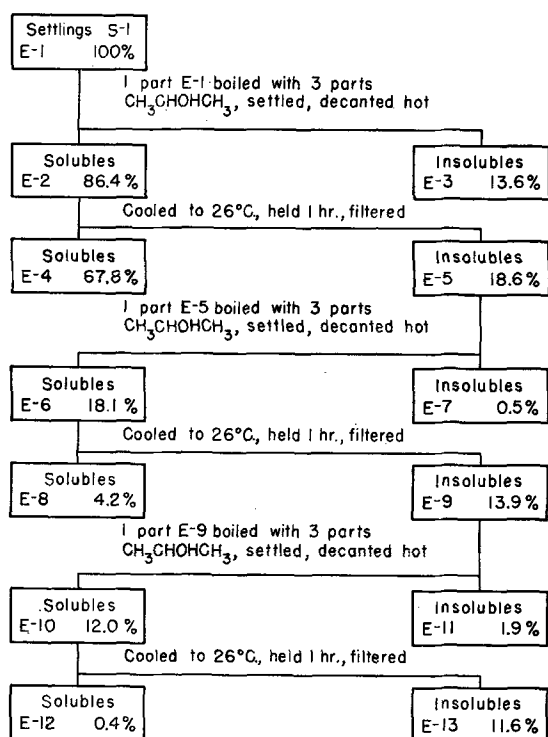
FIG. 5.   Preparation of wax E-13.

sulfuric acid and distilled water. The Gardner color of the bleached, melted sample was 4. The use in the bleaching process of 1 part of chromium trioxide in the place of 0.5 part produced a color of 1.

When a combination of hydrogen peroxide and chromium trioxide (generally 0.5 part of 29% hydrogen peroxide and 1 part of chromium trioxide per 1 part of wax) was used, the bleaching action usually produced a white wax. In such a bleaching the hydrogen peroxide and 40% sulfuric acid were added first and mixed for about 1 hour at 95°C. before the chromium trioxide was added slowly. The spent bleaching reagents were removed as usual by washing the wax successively with a solution of sulfuric acid and water.

Bleaching with chromium trioxide lowered slightly the melting point of a wax, but at the same time it increased the hardness and lowered the iodine value.

Discussion

The procedures described for isolating a hard wax from tank settlings from crude rice bran oil all utilize fractional crystallization from isopropanol as the final step. The use of isopropanol is dictated by several considerations: it is relatively cheap and readily available; at room temperature it is a poor solvent for the hard wax fraction; it boils just above the melting point of the hard wax fraction and is able to dissolve it to a marked extent; and the boiling point of the isopropanol is low enough to permit easy removal from wax and oil. Other alcohols do not possess these advantages to the same degree.

Hydrocarbons like hexane and heptane are inferior to isopropanol as solvents for wax purification in that the wax in the presence of rice bran oil is markedly soluble in these solvents, and in addition such a mixture does not filter readily.

Acetone was the only ketone used in the investigation. For large-scale operations it would be the most logical solvent of this class from the standpoint of cost. Vegetable waxes generally are quite insoluble in acetone, and it has been frequently used in the concentration of wax fractions.

In interpreting the yields reported in Table II, it should be recognized that the tank settlings used were obtained as the byproduct of an operation whose sole object was to obtain oil from rice bran. If the bran had been extracted to obtain both oil and wax, the ratio of hard wax to other components in the settlings would probably have been increased. In obtaining the hard wax fractions listed in the table, fractions of soft wax and of hard wax which might have commercial value were discarded. In such a purification procedure an arbitrary choice must be made as to the portions to be retained. Other factors influencing yields are the filtration and decantation steps which do not produce perfect separations of the solid and liquid phases involved. Separation by centrifugation or washing of the filter cakes would have changed slightly the yields and properties of some of the final products.

The high content of volatiles shown for fraction B-8 (Table II) can be attributed to moisture and alcohol left in the sample because of incomplete drying in air. This sample and the other samples of rice bran wax were tested by heating the powdery form in which they were precipitated from solution. If the samples had first been melted and allowed to re-solidify, their content of volatiles would have been similar to that of carnauba wax.

From the analyses reported in Table II it is evident that tank settlings from crude rice bran oil can be processed in a number of relatively simple ways to produce wax fractions which resemble carnauba wax in important respects, but their properties are not fully equal to the corresponding properties of carnauba wax. The melting and softening points of the fractions are definitely lower by a few degrees. The wax hardness value for each of the products was 100, the maximum reading of the durometer hardness tester, and hence this does not indicate that the samples were of equal hardness. There is no really satisfactory method of measuring this property. However according to the "finger-nail" test, which is commonly used, none of the rice bran waxes was as hard as carnauba.

Each of the purification procedures yielded a hard and non-tacky wax; and insofar as ordinary chemical and physical determinations were concerned, the properties of these waxes were quite similar. Therefore the choice of one procedure over another would depend upon the use to be made of the oil and other byproducts obtained during the processing of the settlings and upon the performance of the waxes in actual formation.

Unfortunately the evaluation of any wax is to a large degree an art. A manufacturer of wax products determines the value of a new wax in accordance to its performance in his products. However it is safe to predict, on the basis of the properties of rice bran wax and upon preliminary testing in actual formulations, that rice bran wax would be a desirable article of commerce and could replace carnauba wax to some extent.

Summary

A typical sample of tank settlings from crude rice bran oil was processed in various ways to obtain a

hard, non-tacky wax fraction. Two procedures investigated consisted of removal of the oil from the tank settlings by washing with acetone, destruction of the phosphatides through hydrolysis or saponification, and subsequent purification by fractionation from isopropanol solution; another involved hydration of the tank settlings, followed by separation of the aqueous and oil phases, and fractionation of the oil phase from isopropanol solution; and two procedures used simple fractionation of the tank settlings with the aid of solvents.

Yield of the hard wax fractions from the typical sample of tank settlings varied from 8.3 to 13.7%, based on the weight of the original settlings. The iodine value varied from 11.1 to 17.6, the free fatty acid content from 2.1 to 7.3%, the phosphorus content from 0.01 to 0.15%. The lowest melting point observed was 75.3°C. and the highest was 79.9.

The samples of hard wax were almost black in color when in the liquid state and could not be bleached readily with activated clay or carbon. The waxes were bleached readily by hydrogen peroxide and by chromium trioxide in the presence of sulfuric acid solution, or by combinations of these reagents. Practically white waxes could be produced with 0.5 part of 29% hydrogen peroxide and 1 part of chromium trioxide per 1 part of wax.

REFERENCES

1. American Oil Chemists' Society, "Official and Tentative Methods," 2nd ed., edited by V. C. Mehlenbacher, Chicago, 1946.
2. Gardner, H. A., "Physical and Chemical Examination of Paints, Varnishes, Lacquers, and Colors," 10th ed., Inst. Paint and Varnish Research, Bethesda, Md., 1946.
3. Johnson, G. W., (to I. G. Farbenindustrie Aktiengesellschaft) Brit. Pat. 488,381 (1938).
4. Kimm, R. H., Sci. Papers Inst. Phys. Chem. Research (Tokyo), 34, 637-677 (1938).
5. Murray, K. E., and Schonfeld, R., J. Am. Oil Chem. Soc., 28, 461-466 (1951).
6. Norbi, Hiroso, J. Soc. Chem. Ind. Japan, 46, 15-17 (1943).
7. Pons, W. A. Jr., and Guthrie, J. D., Ind. Eng. Chem., Anal. Ed., 18, 184-186 (1946).
8. Reddi, P. B. V., Murti, K. S., and Feuge, R. O., J. Am. Oil Chem. Soc., 25, 206-211 (1948).
9. Report in Chem. and Ind., 58, 1014 (1939).
10. Tsuchiya, Tomotaro, J. Nippon Oil Technol. Soc., 1, No. 1, 1-6 (1948).
11. Ueno, Seiichi, Matsuda, Sumio, and Kimura, Taha, J. Soc. Chem. Ind. Japan, 47, 604-607 (1944).
12. Ueno, Seiichi, Matsuda, Sumio, and Okada, Joshio, J. Soc. Chem. Ind. Japan, 44, 687-689 (1941).
13. Unpublished report of a Japanese process for purifying and hydrogenating rice bran wax.
14. Warth, A. H., "The Chemistry and Technology of Waxes," Reinhold Publishing Corporation, New York, 1947, p. 332.
15. Yamazaki, Riichiro, and Ogawa, Goro, J. Soc. Chem. Ind. Japan, 44, Suppl. binding 241 (1941).

[Received May 26, 1952]

Solubilization of Orange OT and Dimethylaminoazobenzene

M. WESLEY RIGG and FRED W. J. LIU,[2] Department of Chemistry, Temple University, Philadelphia, Pennsylvania

SOLUBILIZATION, a fundamental phenomenon associated with colloidal aggregates, i.e., miscelles, has been investigated by numerous workers (2, 4, 7, 12). The measurement of solubilization by the dye solubility method appears to be convenient. However considerable variation is to be found in the results reported by different workers. For example, the earlier work reported by McBain and co-workers (2, 10) is found to be at variance with that reported by Kolthoff and Stricks (7). It is our purpose to reinvestigate the dye method with emphasis on the reported points of disagreement.

It was thought that departure from neutrality of the soap solution might account for the divergent results, hence the effect of a slight excess both acid and alkali in Na- and K-laurates was studied. The interesting possibility of the existence of micelles below the critical micelle concentration will be discussed in light of the present work.

Materials Used

Orange OT (F.D. and C. No. 2,1-o-tolyl-azo-2-naphthol), a Calco product, was purified according to directions given by McBain (10).

Dimethylaminoazobenzene (abbreviated as DMAB), a Merck technical product, was recrystallized according to Kolthoff's directions (7).

Potassium and sodium laurate solutions were prepared from Eastman Kodak white label lauric acid and KOH and NaOH solutions (carbonate free), respectively. Solutions were prepared with excess lauric acid (1.6% in Na-laurate and 1.2% in K-laurate) and with excess alkali (1.4% in NaOH and 0.74% in KOH).

Sodium oleate, Baker C.P. neutral grade, was used without further purification.

Dodecylamine hydrochloride (DDA.HCl) was prepared by neutralization of the free DDA (Armour product), dissolved in absolute ethanol, with concentrated HCl. After cooling to 0°C., the white mass of DDA.HCl crystals was filtered, washed first with ether and then with ethanol, and then dried in vacuo at room temperature. Analysis for ionizable chloride indicated 99% purity.

Span 20 and Tween 20 were obtained from the Atlas Powder Company and dried at 100°C. for 7 hours before use.

N-Dodecyl-β-alanine hydrochloride was prepared in the same way as DDA.HCl by neutralization of N-dodecyl-β-alanine (G. E. Goodrich product).

Tergitol 4 was obtained from the Union Carbide and Carbon Corporation.

Ultrawet K was obtained from the Atlantic Refining Company.

Technique and Experimental Method

Detergent solutions of varying concentrations were placed in 30-ml. vaccine bottles, with sufficient dye to