9. Determine moisture in average lint removed at intervals, recording as C.

D. CALCULATION

The residual lint, that is, the lint remaining on the original sample of seed, is conventionally calculated to an 8% moisture basis.

Therefore when 50-g. sample is used

$$\text{Percentage lint} = 2(A - B) \times \frac{100 - C}{92}$$

Summary

The several advantages of the infrared method over the official method Aa 7-44 are as follows:

1. In the infrared method an error in the original weight of the seed is reflected only as that percentage lint of the errata from the 50 g. In the present official method such an error is doubled in the final percentage.

2. An error in the original moisture determination is reflected as an equal error of lint percentage when the official method is used. In the infrared method the original moisture percentage does not enter into the calculation, and therefore such an error is not reflected.

3. A single oven for the infrared method, as compared to three required for the official method (one drying, one fuming, and one overnight drying).

4. Power consumption is substantially less as a result of the reduced total oven time of from 18 or 20 hrs. to 35 min. Actual cost varies with KWH rates. Duplicate determinations may be expected to use about .1 KWH.

5. Reduction of HCl by 50%, which also results in less breakage of hull during brushing.

6. Reduced cost of containers required for the determinations.

THE basic procedure was presented to the subcommittee on residual linters for study in the early months of 1954. During the months that followed many determinations were made through the collaborative effort of the subcommittee. In addition, some of the individual laboratories accumulated data comparing results of the infrared method to those of the official method. A typical portion of the data thus obtained was reported to the subcommittee for tabulation and evaluation.

The close agreement obtained between duplicate determinations of many thousands of samples and the reproducibility of the infrared method warrants adoption as an official method.

NOTE: Preliminary study leads to the belief that it is possible to substitute the infrared method of treatment reported here for the present pre-drying and lint hydrolysis procedure of the A.O.C.S. Official Methods (Aa 4-38 and Aa 5-38) for the analysis of cottonseed for oil and ammonia (N equivalent).

Further investigation of this possibility is being carried on in these laboratories. If successful, it will be the first important improvement and change in cottonseed analysis since the present official method was announced in 1928.

Effect of Heat on the Color of Trichloroethylene-Extracted Cottonseed Oil

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PREVIOUS WORK in this laboratory (5) has shown that the color of trichloroethylene-extracted cottonseed oil extracted and desolventized in the pilot plant equipment under conditions producing a very satisfactory soybean oil and refined by the ordinary refining method is too dark to be acceptable. Duncan (2) has reported that a prime oil can be produced by extraction with trichloroethylene but gave no operating conditions. Vix, Pollard, Spadaro, and Gastrock (6), after a systematic study of the effect of heat on hexane-cottonseed oil miscellas, reported that color fixation became objectionable between 150° and 180°F. and that beyond 180°F. it increased rapidly. The present studies were for the purpose of obtaining similar data for trichloroethylene-cottonseed oil miscellas to determine whether the effect of heat is similar with the two solvents, that is, whether it is primarily a heat effect.

Effect of Desolventization Temperature on the Color of the Oil

The Miscella. Prime delinted cottonseed were dehulled, flaked, and extracted with trichloroethylene at room temperature in the countercurrent extractor described by Arnold and P'Pool (1) to produce the miscella.

Desolventizing the Miscella. The miscella was desolventized in the equipment, shown in the flow sheet in Figure 1, consisting essentially of a climbing film evaporator and a packed steam-stripping column, together with the necessary auxiliary equipment. The evaporator consisted of a ⅜-in. pipe, 6 ft. long, heated by an electric-resistance wire-winding controlled by a variable transformer. This evaporator discharged into a flash chamber, from which the hot concentrated miscella flowed by gravity through a pre-heater into the stripping column.

This stripping column was a 2-in. glass pipe packed with a 4-ft. bed of ½-in. Berl saddles and heated by electric-resistance wire. Stripping steam was generated from distilled water in a steam-jacketed pipe still and superheated in an electrically heated pipe. The equipment was operated under reduced pressure produced by a water jet ejector and controlled by air bleed-in valves.

Results. Batches of the miscella were desolventized at four temperature ranges: 150°–160°F.; 170°–180°
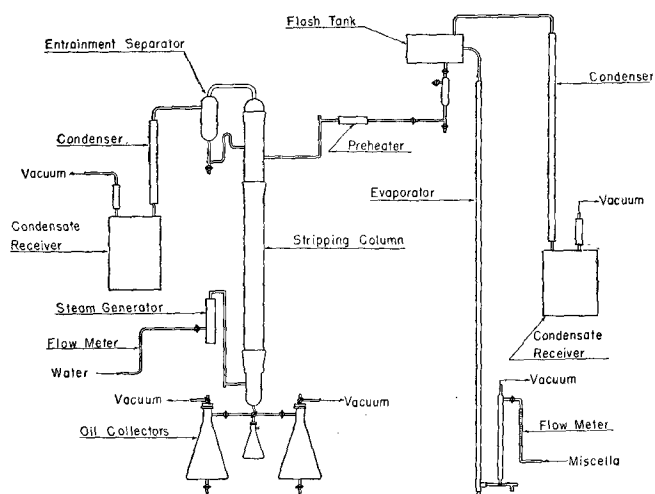
FIG. 1. Apparatus used for concentrating and stripping the miscella.

F.; 200°–210°F.; and 240°–250°F. The resulting oil was refined and bleached by the official method for slow break oil (4). Free fatty acid ranged from 1.00 to 1.10% and refining loss from 5.62 to 8.92%. The gossypol content of the oil was 1.75%. The effect of temperature on color is shown in Figure 2. Color determinations were made by the standard method, using a spectrophotometer.

The results indicate that the effect of desolventizing temperature on prime trichloroethylene-extracted cottonseed oil is similar to that obtained previously with hexane-extracted oil by Vix, Pollard, Spadaro, and Gastrock (6). In addition, previous work in this laboratory by Liu (3) with miscella produced by the extraction of cottonseed meats which had deteriorated sufficiently in storage to produce a low grade of oil showed a similar darkening trend when desolventized at temperatures from 130° to 230°F. Liu also found that allowing the miscella to stand six to ten weeks before desolventizing caused the oil to darken considerably.

Effect of Extraction Temperature on Oil Color

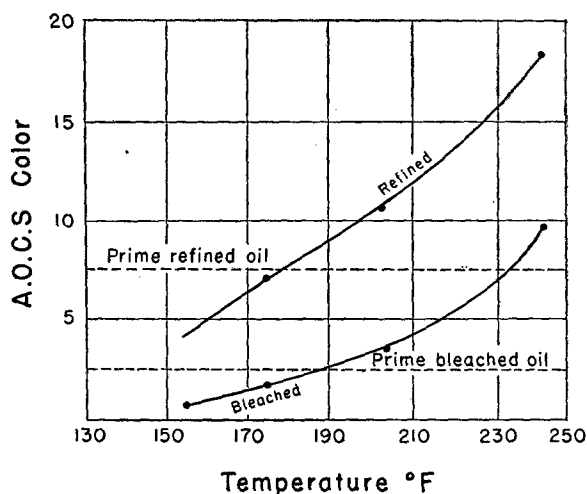Since it is desirable to maintain as high an extraction temperature as practical, it is desirable to know the effect of extraction temperatures on oil color. Five extractions were made in the countercurrent extractor (1) from the same batch of prime flakes varying the extraction temperature from 78° to 168°F. The following constant data applied to all runs: average flake thickness, 0.0133 in.; extraction time, 25.5 min.; flake moisture content, 6.44%; free gossypol content of flakes, 1.69; and meat temperature before flaking, 155°F. The results shown in Figure 3 indicate the desirability of keeping the extraction temperature low.
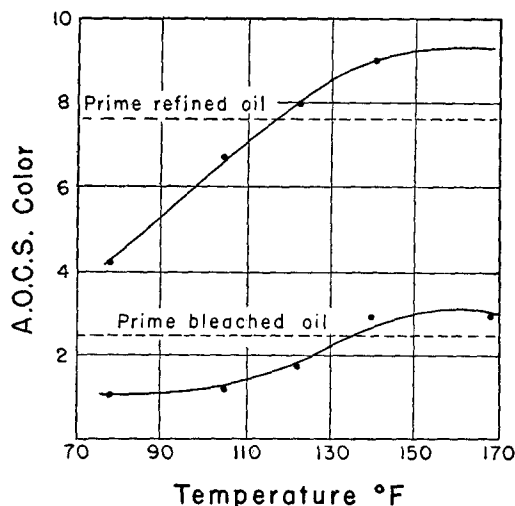

FIG. 3. Effect of extraction temperature on the color of tri-chloroethylene-extracted cottonseed oil.

Effect of Other Temperature Variables on Oil Color

Temperature of Meats before Flaking. Some heating of the meats prior to flaking is desirable to render them more plastic so that they will undergo the flaking operation with less disintegration. Since good flakes can be made from meats heated to 150°F., this temperature was used in most of the extractions. To determine the effect of higher temperatures on the color of the oil, batches of meats from prime seed were heated at 168°, 175°, 181°, 203°F., flaked, and extracted at 122°F. The miscella was desolventized at 170°–180°F. The corresponding A.O.C.S. colors for the resulting refined oils were 5.51, 8.64, 8.31, and 12.89. Bleached oil color varied inconsistently between 2.65 and 4.22.

Miscella Concentration. Data from three runs, in which the concentration of the miscella from the extractor was the only variable, show a decrease in color for refined oil from 9.58 to 4.93 and for bleached oil from 1.51 to 0.57 with an increase in oil content of the miscella from 11.28 to 44.90%. It seems probable that this is a time-temperature effect; the dilute miscella requires a longer desolventization treatment than the more concentrated material.

Discussion

The similarity of the effect of heat during the desolventization of hexane miscellas as found by Vix, Pollard, Spadaro, and Gastrock (6) and of trichloroethylene miscellas, as shown in this paper, indicates that the darkening is caused primarily by heat, rather than solvent. The time required in desolventization is also important and should be kept at a minimum.

FIG. 2. Effect of desolventizing temperature on the color of trichloroethylene-extracted cottonseed oil.

Extraction temperature should be kept low for good color although higher temperatures result in better extraction efficiency. Heating the meats to a high temperature, while considered an advantage in pressure removal of the oil, causes both poor color and lowered extraction efficiency in trichloroethylene extraction of cottonseed oil.

The toxicity to cattle of certain batches of trichloroethylene-extracted soybean oil meal has raised the question of possible toxicity of other products extracted by trichloroethylene. Since the work presented in this paper was a study in extraction only, the use of trichloroethylene as an experimental solvent should not be construed as a recommendation by the authors that the product resulting from this extraction is or is not suitable as a feed.

Summary

Trichloroethylene cottonseed oil miscellas from prime meats heated during desolventization above 180°F. produced a refined oil darker than prime.

When the miscellas were heated above 190°F., the bleached oils produced from them were darker than prime. Extracting prime meats with trichloroethylene above 118°F. produced an oil darker than prime. There is some evidence that heating the meats above about 170°F. also gives a dark oil. Dilute miscellas, when desolventized, produced a darker oil than more concentrated ones probably because of the longer time required for solvent removal. It is believed that the darkening is primarily a function of time and temperature, rather than the solvent used.

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Micelle Formation and Solubilization in Nonaqueous Solvents

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OIL-SOLUBLE SOAPS have been familiar industrial materials for many years, and the colloidal nature of their dispersions in oils was early recognized (4, 8, 12, 16, 25, 53). It is only within the past 10 years however that much information has become available concerning the exact state in which such substances exist in nonpolar solvents. This paper will discuss some aspects of micelle formation in nonpolar solvents in the light of the published data and of hitherto unpublished results from the Naval Research Laboratory.

For the purposes of this discussion the term micelle will be taken to mean any thermodynamically stable association colloid formed by three or more amphipathic molecules. One dimension of such a structure will usually, in a nonpolar solvent, be comparable with twice the length of the monomer unit. Because some soaps show a continuous transition from small spheres of less than 50 monomer units to polymer-like linear structures containing many hundreds of molecules, it will be convenient to extend the term micelle, and our consideration of the micellar state, to the chain-like structures exhibited by aluminum soaps and by the arylstearate soaps. The liquid crystalline systems formed in many concentrated soap-oil systems will not be considered although some elements of similarity exist. Emulsions also will not be considered although there may be cases in which micelles pass smoothly into emulsion droplets as the amount of water solubilized by the micelle becomes large as compared with the amount of soap present.

It will be convenient, although inexact, to use the term soap as a generic name for the ionic amphipaths which form micelles in oil. The term oil-soluble soap is also a misnomer but has been established by long usage; it will be used here to refer to a soap micellarly dispersible in a nonpolar solvent.

Micelle formation in nonpolar solvents has been demonstrated for the following classes of compounds:

a) alkali and alkaline earth soaps of naphthenic and sulfonic acids from petroleum and of related synthetic substances, such as the arylstearic and alkylnaphthalene sulfonic acids (2, 22, 28, 37, 36, 55);

b) oleates, naphthenates, and various C_8–C_{18} normal fatty acid soaps of the heavy metals, including copper, zinc, iron, nickel, and cobalt (8, 25, 35, 40, 53, 54);

c) aluminum soaps of oleic, 2-ethylhexanoic, naphthenic, and C_8–C_{18} normal fatty acids (18, 33, 34, 51);

d) quaternary ammonium salts of a suitable cation with an anion of relatively small volume (10, 14, 29, 48);

e) alkali and alkaline earth alkylphenolates, and alkylphosphates (44); and

f) nonionic surface active substances such as hexanolamine oleate, nonaethylene glycol monolaurate, mannitan mono-oleate, and certain alkyd resins (17, 43, 47, 50).

Micelle formation by soaps in aqueous solution has been studied so extensively and fruitfully that there is a natural tendency to reason about nonaqueous micelles by analogy from aqueous phenomena. The basic structures of the two types of micelle however are so diametrically opposite that such reasoning may be unsafe. In the nonaqueous micelles the polar portions of the amphipathic molecule are buried in the central core, rather than distributed over the outer surface as in aqueous systems. While the oil-soluble soaps are still strongly ionic, they are not appreciably dissociated in oil, and the micelle carries no net charge comparable with that of aqueous soap micelles. In aqueous systems soap micelle size is considered to be limited by the accumulation of charged ions in the micelle, which prevents the approach of further ions; in nonaqueous systems one must look elsewhere for the mechanism that stops micelle growth before precipitation can occur. The major energy available for micelle formation in a hydrocarbon solvent comes from the interaction of the polar heads, either as a generalized dipole attraction or by the formation of specific atom to atom coordination or hydrogen bonds, whereas in aqueous micelles the driving force may be considered to be the decrease in free energy possible