tions Board, in the establishment of suitable purchase standards for the use of the Federal Government.

The Bureau experts are members of nearly all of our seventy technical committees; and the chairmanship of twenty-seven of these committees is held by Bureau experts.

These specifications for Government use are adopted only after careful consideration of all pertinent commercial specifications, as it is realized that the selection of a specification or standard without due regard to the manufacturing problems involved would be as serious as for manufacturers to establish them without a careful consideration of the needs of the purchaser. In the selection of specifications for Government use the Federal Specifications Board is coördinating these two interests in a manner which is fair to and understood by both the manufacturer and the user, and will in time base all Government purchases on correct standards of quality and practice. This procedure will, no doubt, serve in time as a model to be followed by large corporations, municipalities, States and the public. In fact, several such cases have already occurred.

In case your society or any group of manufacturers associated therewith, has any problems to the solution of which the Bureau of Standards might be able to contribute, we earnestly invite your attention to the advantages of establishing a research associate at the Bureau.

U. S. Bureau of Standards
Washington, D. C.

CONSTITUENTS OF CRUDE COTTONSEED OIL*

By George S. Jamieson and Walter F. Baughman

This paper reports further progress in the investigation assigned to the Oil, Fat, and Wax Laboratory at the conference of the Basic Research-Committee and the Department of Agriculture, September, 1921.[1]

The authors endeavored to obtain more definite information in regard to the presence of the so-called vegetable mucilage in crude cottonseed oil. For convenience, the "settlings," which separates when the crude oil is permitted to stand several weeks after expression, was examined. The "settlings" from a 5-gallon sample of crude oil was repeatedly extracted with acetone. The insoluble portion of the "settlings" was ground to a powder after the removal of the acetone, and about 125 g. was boiled with 250 cc. of absolute alcohol for several hours in a flask connected with a return condenser. This treatment was repeated with two more 250-cc.

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[1] Previous reports: *The Cotton Oil Press*, **6** (No. 4), 33; **7** (No. 2), 35; **7** (No. 5), 29; This Journal, **1**, 30.

portions of alcohol. Then the insoluble residue was transferred to a Büchner funnel, thoroughly washed with alcohol, and air dried. It was found that the alcohol dissolved about 34% of the acetone-insoluble settlings. An experiment made several years ago with the acetone-insoluble "settlings" from another sample of crude cottonseed oil gave about 31% of alcohol-soluble constituents.

The alcohol-insoluble portion of the "settlings" was placed in several paper extraction thimbles and extracted with boiling water in order to remove the mucilage. After about an hour the extraction stopped, owing to the clogging of the pores of the thimbles. Consequently a quantitative determination of the water-soluble substances could not be made. Other procedures, which had been tried previously, were even less satisfactory.[2] The aqueous extract was neutral in reaction. A 20% solution of normal lead acetate was added in excess, and the slightly colored lead salt which separated was filtered and thoroughly washed with water. The filtrate was reserved for examination. The lead salt was suspended in water and decomposed with hydrogen sulfide. After removing the lead sulfide, the filtrate was concentrated to a volume of about 10 cc. on the steam bath and cooled to room temperature. Upon adding 30 cc. of alcohol to this solution, a white gelatinous precipitate of the mucilage was obtained. Qualitative tests showed that it contained small quantities of calcium, magnesium, and phosphorus. When a small quantity of it was added to refined cottonseed oil and the mixture stirred with water, an emulsion was readily formed, which showed no evidence of breaking after being kept for 2 days. It is evident that this substance, which causes emulsions so easily, is a factor in the retention of neutral oil in the soap stock obtained in refining the crude oil. Even if a crude oil is held until the "settlings" has separated before it is refined, it will still contain a considerable quantity of unprecipitated "settlings," the larger part of which can be precipitated by agitating and heating the oil with 2 or 3% of water. However, no practicable method has yet been devised for removing from the oil the substances precipitated by treatment with water prior to the caustic soda refining.[3]

Although it has not been possible to determine the quantity of mucilage in a crude cottonseed oil, it is believed that it constitutes only a very small part of the non-glyceride substances present. This is particularly fortunate in view of its emulsifying powers.

Basic lead acetate was added to the filtrate from the lead salt of the mucilage. No precipitate was formed, which shows the absence of water-soluble gum in the "settlings." The lead was removed as sulfide, and the filtrate was concentrated to a small volume. A somewhat thick brown

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[2] *The Cotton Oil Press*, **7** (No. 5), 29.

[3] THIS JOURNAL, **1**, 34.

sirup, with an odor resembling that of roast beef, was obtained. It gave very strong tests for calcium, magnesium, and phosphorus after thorough digestion with concentrated nitric acid. This indicates that the water-soluble portion of the "settlings" contains organic phospho-compounds, which are not precipitated by either normal or basic lead acetate.

In order to compare this so-called mucilage with that which might be obtained directly from cottonseed, about 2 pounds of ground decorticated seed was heated to about 75°C. with water for about 2 hours. The mixture, while hot, was pressed in a cloth bag. About 500 cc. of the solution was boiled for a few minutes to precipitate the proteins and filtered. A portion of the filtrate, made very faintly acid with acetic acid and boiled, gave no further precipitation of protein. An excess of a 20% solution of lead acetate was added to the filtrate. The voluminous light-colored lead salt was filtered and thoroughly washed with water, and the lead was removed as sulfide as previously described. After the concentration of the filtrate to about 20 cc., the mucilage was precipitated by the addition of 80 cc. of 95% alcohol. This voluminous white precipitate was filtered and repeatedly washed with alcohol. Like the corresponding precipitate obtained from the "settlings," it contained small quantities of calcium, magnesium and phosphorus. When a small quantity was stirred with refined cottonseed oil and water, a very persistent emulsion quickly formed. The mucilage obtained from the settlings appears to be identical with that obtained directly from the cottonseed.

The acetone extract of the "settlings" was concentrated by distillation until the larger part of the solvent was removed; it was then allowed to stand for about 2 weeks at room temperature. A crystalline substance, which had separated from the solution, was removed and recrystallized twice from alcohol. About 2 g. of the purified product, which melted at 69° to 70°C. and proved to be stearic acid, was obtained. Stearic acid was also obtained from a concentrated alcoholic extract of the oil separated from the "settlings" which had stood for some weeks. Further concentration of this alcoholic solution gave a small quantity of palmitic acid. This is further proof that the free fatty acids in oils contain saturated acids[4] in addition to unsaturated acids.

It was suggested that a study of the substances which color cottonseed oil be included in the investigation. Part of the color of the crude oil is due to resin,[5] which is removed from the oil when it is refined by caustic soda. It was formerly believed that gossypol, which, if present in any quantity, would naturally contribute greatly to the color of the oil, gave crude oil its red color. Repeated examination of commercial crude oils, however, has shown that they contain no gossypol.

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[4] *The Cotton Oil Press*, **7** (No. 2), 35.

[5] *The Cotton Oil Press*, **7** (No. 5), 29.

So far as can be ascertained, there is no method whereby any of the so-called pigments, such as carotin, can be separated from an oil in a form which will serve for their subsequent identification. Apparently the only practical line of attack is by means of the spectrophotometer. As is generally known, Dr. Priest has obtained some definite results in connection with the measurement of the color of oils and the identification of some of the pigments. Therefore, this phase of the investigation belongs more properly to the physicist than to the chemist.

Refining the oil with caustic soda is the only known method for removing all the resin from the oil. No procedure for the separation of the saponified resin from the soap stock has been found, however. Experiments have shown that a portion of the resin separates with the "settlings" when the oil is permitted to stand for a few weeks after expression. Agitating and heating the oil after the removal of the "settlings" with 2 or 3% of water gives a further separation of rosin with other substances. The extraction of the oil which has been treated with water by alcohol will remove more of the resin. The water and alcohol treatments lighten the color of the oil believed to be due to the removal of resin, although it is still red. The resin separated from an alcoholic extract of the oil or the "settlings" is a dark red brown.

A small portion of the resin was dissolved in 50 cc. of warm alcohol. The solution was cooled in an ice bath for an hour with frequent agitation, then filtered to remove a minute quantity of insoluble matter. A small quantity of the solution was tested with an alcoholic solution of cadmium chloride for lecithin, etc., but no precipitate formed. Another portion, to which 10 volumes of acetone was added, also gave no precipitate. An alcoholic solution of copper acetate was added in slight excess to the remainder of the alcoholic solution of the resin. A dark yellow flocculent precipitate separated. This was removed by filtration and thoroughly washed with alcohol and ether. The filtrate, which had been kept separate from the washings, was light yellow, while the original solution of the resin was strongly reddish yellow. The filtrate was heated to boiling, and another small quantity of the copper resinate was obtained. The filtrate was evaporated to dryness. In addition to the resin not precipitated as the copper salt, a considerable quantity of phospho-organic substances, which were not precipitated from the alcoholic solution by cadmium chloride, copper acetate, or a large quantity of acetone, remained in the residue. An analysis of the copper salt dried for several days in an evacuated desiccator showed that it contained 18.4% of copper. The copper salt of the resin from another sample of oil contained 16.7% of copper. It has been found that after the precipitation of the phosphatides by cadmium chloride from the concentrated alcoholic extract of the crude oil a part of the resin can be precipitated by copper acetate. If copper salts of the free fatty acids separate (by adding too much copper acetate solution) with the copper resinate, as indicated by their strong green color, they can usually be removed from the resinate by repeated treatment with ether.

Examination showed that several preparations of these copper salts contained small quantities of calcium, magnesium, and organic phosphorus compounds. In view of the fact that each preparation of the copper resinate had been thoroughly washed with alcohol and ether, it seems probable that a small quantity of an insoluble copper salt of some phosphatide had precipitated with the copper resinate.

Summary

A small quantity of so-called vegetable mucilage was separated from crude cottonseed oil. It was precipitated from an aqueous solution by normal lead acetate. No water-soluble gum could be detected. Experiments showed that this mucilage readily emulsifies the oil with water and that the emulsion does not break after standing for several days. It is believed that the mucilage constitutes only a very small part of the non-glyceride substances present in the oil.

Treating the oil with water and then extracting the separated oil repeatedly with large volumes of alcohol only removes part of the resin. The resin is partially removed from an alcoholic solution by an alcoholic solution of copper acetate in the form of a dark yellow flocculent precipitate. The copper salt is insoluble in alcohol and ether. It is believed that part of the deep red color of the crude oil is due to this resin.

A Contribution from the Oil, Fat and Wax Laboratory
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