SHORT COMMUNICATION

Some Practical Aspects Connected with the Presence of Calcium in Soybean Oils

ABSTRACT

Presence of calcium in crude and degummed soybean oils prevents complete elimination of phosphatides by hydration and enhances the formation of heavy precipitates. They block industrial centrifuges at the later stages of the refining processes. Industrially extracted degummed soybean oils contain appreciable amounts of calcium (ca. 100 ppm) and its source was traced to the processed soybeans. Various pre-extraction treatments of the soybeans in industry augment the calcium content in the oils, since crude Soxhlet-extracted soybean oils contained only 15 ppm calcium. Additions at the alkali-refining stages of EDTA or of polyphosphate, to stabilize aqueous suspensions which also contain calcium salts, are suggested as a partial remedy to the frequent blocking of the centrifuges.

Many oil refining plants which pretreat degummed soybean oil (prior to neutralization) with ca. 0.1% concentrated phosphoric acid suffer from blocking of centrifuges that separate the soap from the neutralized soybean oil. This blocking is caused by large amounts of hard precipitate. According to Braae (1), such a phosphoric acid pretreatment reduces the phosphatides content in refined soybean oil, decreases the refining losses and also prevents to a large degree the formation of off-flavors in the refined oils. We have worked to determine the cause of the precipitate and to find ways to prevent its formation.

Analyses of various precipitates show big variations in composition. These variations were found even in different layers of a particular precipitate. The ranges of the constituents were 22-45% ash, 6-25% fatty material (mostly soaps) and 40-70% moisture. The ash contained 4-12% calcium and 14-23% phosphorus as $(PO_4)^{3-}$. The precipitates were yellowish due to the presence of iron, but only traces of iron (ca. 0.01%) were found.

These data indicate that the precipitates contain calcium phosphates as a main component. The source of calcium in the precipitates was sought. The water and the reagents used for treatment of the oil were found to be calcium-free. Calcium contents of soybean oils from two stages of the refining process and of a laboratory hexane-extracted oil (determined by atomic absorption spectrophotometry) were 100 ppm in industrially degummed, 1 ppm in industrially alkali-refined, and 15 ppm in crude laboratory-extracted (Soxhlet). Thus industrially alkali-refined oils were found practically free of calcium; the latter is efficiently removed by the neutralization processes. Crude soybean oil from soybeans ground in a mortar and extracted in a Soxhlet with petroleum ether in the laboratory, contained much less calcium than the industrially degummed soybean oil (15 vs. 100 ppm, see above). Calculation (based on the above results) shows that precipitation of calcium ions by the phosphoric acid treatment would yield 2.6 kg anhydrous $Ca_3(PO_4)_2$/10 tons degummed soybean oil with calcium content of 100 ppm. This amount of calcium phosphates might form the core for the precipitate which could include other substances.

While these experiments were being performed, a paper by A. Hvolby (2) was published in which he discussed the connection between the presence of calcium and magnesium in soybean oil and the amount of nonhydratable phosphatides. Calcium content in soybean oils (after first degumming) was reported as 83-135 ppm, similar to the content of calcium found by us (100 ppm). Soybeans are reported (3) to contain an average of 0.27% ca, on dry basis. The industrial conditioning before extraction must lead to the comparatively high level of calcium in the industrially extracted oils. One cannot expect that the mode of the various industrial pre-extraction treatments of the soybeans will be changed in order to reduce the calcium content in degummed soybean oils and the amount of hard precipitates. Efforts to diminish the amount of precipitates should be directed toward applying another agent for treatment of degummed soybean oils before neutralization, instead of phosphoric acid, or toward applying an additional agent during the neutralization step.

Hvolby (2) treated directly degummed soybean oil with a large volume of EDTA solution (1 part of oil per 8 parts of 10% EDTA at pH 10 for 2 hr at 20 C), to bind calcium and to precipitate the phosphatidic acids. He succeeded in removing all the phosphatides and all the calcium from the degummed oil. By a direct treatment of soybean oil with saturated sodium pyrophosphate solution (at the same v/v as above) he removed ca. 90% of the nonhydratable phosphatides. In the industry, however, such large volumes of reagents per volume of oil do not seem feasible.

In preliminary experiments, suspensions of centrifuge precipitates in water and in solutions of sodium chloride or sodium hydroxide, were stabilized by additions of EDTA or of sodium polyphosphate (1 part per 10 parts of precipitate). EDTA was more efficient than the polyphosphate. The stabilized aqueous suspensions required longer times or higher accelerations, or both, in order to remove the precipitate by centrifugation. Such a treatment might be of use in the industry and can be applied either instead of or together with the phosphoric acid treatment. Further experimental work is required.

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REFERENCES

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