Gaseous Ammonia as a Refining Agent for Cottonseed Oils[1]

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Abstract

In this investigation the application of gaseous ammonia to cottonseed oil refining was explored. The ammonia reacted quantitatively with the free fatty acids in the oil; its solubility in cottonseed oil was determined as a function of pressure. In "degumming" it was more efficient in removing phosphatides than other agents.

A reduction in refining loss resulted for oils refined with gaseous ammonia as outlined and compared with the standard AOCS cup loss analysis. However, the oil colors were substantially higher even though the ammonia treated oils were re-refined with caustic solution. Results using cottonseed oil-hexane "miscellas" containing less than 70% oil showed low refining losses, but the colors were extremely high. Above 70% oil content the losses were higher, but the colors were lower. The colors never equalled "standard cup" results.

Introduction

THE MOST IMPORTANT and generally practiced method of refining cottonseed oil is to treat the crude oil with an alkali. Alkali refining effects an almost complete removal of free fatty acids by converting them to oil insoluble soaps. Other acidic substances likewise combine with the alkali and there is some removal of impurities from the oil by adsorption by the soap formed in the operation. Substances such as phosphatides which become insoluble by hydration are also removed.

The presence of phosphatides leads to a loss by entrainment of some neutral oil. This fact is generally attributed to their emulsifying nature. A pre-refining treatment to remove the phosphatides, called degumming (1), has proven to be successful at some locations. Degumming of oils intended for edible use is accomplished by hydrating the phosphatides to make them insoluble in the oil and then centrifuging to separate the hydrated gums.

The technology of alkali refining is concerned with the proper choice of alkali, amount of alkali, and refining technique to produce the desired purification without excessive loss of oil.

The alkali most commonly employed for refining oils is caustic soda, which is much more effective in its decolorizing action than weaker alkalies. However, caustic soda has the disadvantage of saponifying a small portion of the oil, in addition to reacting with the free fatty acids. Weak alkalies such as soda ash or ammonium hydroxide are capable of reacting with the free fatty acids without attacking the oil, but they have little or no effect on color bodies.

The above features suggested that a two-step refining process might be useful. Such a process would use a weak alkali to neutralize and remove the fatty acids and would then use a strong alkali such as caustic soda to remove the color bodies. One such process, the Clayton process, has been in commercial operation since 1938 (2,3). The weak alkali is soda ash while the strong alkali is caustic soda.

The use of ammonium hydroxide as the weak alkali has met with little application because of the formation of emulsions which are difficult to separate. In 1932, Rosenstein and Hund (4) patented a method in which a mixture of monoethanolamine and ammonium hydroxide is used to refine a continuous flow of vegetable oil. In 1941, Van Dijick (5) described a process for the use of ammonium hydroxide to refine palm oil in a multistage countercurrent extraction with aqueous isopropyl alcohol. More recently Clayton (6) described a method in which 14% ammonium hydroxide is used in refining crude soybean oil at 150F. The ammonium soaps are hydrated with excess water and separated from the neutralized oil. The ammonium soap is vacuum distilled to give free fatty acid and gums while the ammonia is distilled off for reuse. The soapstock resulting from this process has an acetone insoluble (phospholipid) portion of 75% as compared to 62% in water degumming. The neutralized oil produced requires only a quick caustic wash to give a good quality edible oil. In a later patent (7) Clayton uses 1 to 3.5% by weight of 1.5 to 29% ammonium hydroxide to refine soybean oil. The well-mixed oil and ammonia solution is heated to 200F., and then rapidly cooled to 150F., and finally centrifuged to separate gums and soaps. This process yields gums of as high quality as those in his previous patent.

Recently the attention of industry has been drawn to the alkali refining of the oil-hexane solution called "miscella" which is obtained by solvent extraction of oil. Here again the two-step refining process, using both soda ash and ammonium hydroxide has been studied (8,9,10).

Gaseous ammonia was suggested for treatment of cottonseed while in storage (11). It reduces the heating of the seed and inhibits the formation of free fatty acids during storage. The color of the extracted oil becomes lighter.

Although pure ammonia is relatively inexpensive, no information other than patent literature (6) about the use of gaseous or anhydrous liquid ammonia for the degumming or refining of crude vegetable oils was found. The objective of the present investigation was to study the applications of gaseous ammonia to cottonseed oil refining.

Experimental

Gaseous ammonia refining was accomplished in a centrifuge bottle adapted as shown in Figure 1. The cover was made of a lower ring which fitted around the neck of the bottle, and the upper ring which was fastened to the lower ring by two screws. Two stainless steel tubes passed through the upper ring. The long one was connected to an ammonia cylinder and the short one was used as a vent.

A sample of 100 g of oil or 150 g of miscella was placed in the centrifuge bottle and the bottle was pressurized with ammonia at 8 psig. The assembly was agitated by shaking for 15 min at 35C while the ammonia pressure was maintained. It was then handled as described later.

A rapid reaction took place with the formation of ammonium soap as a gel which could not be separated by centrifuging. Experimentation with the oil-soap
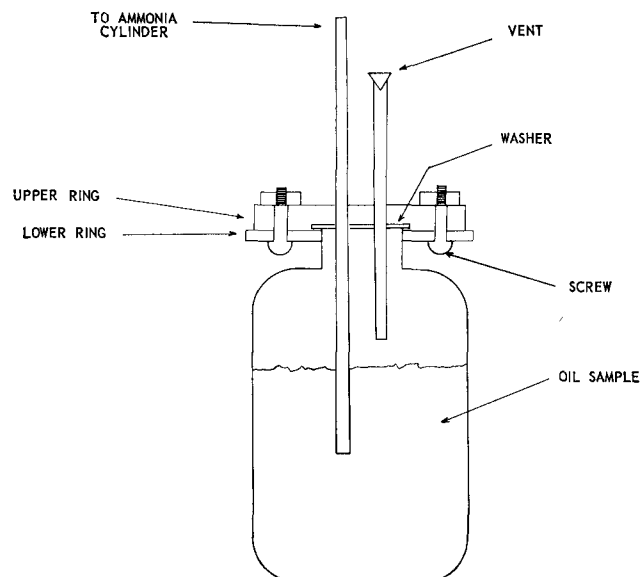
FIG. 1. Centrifuge bottle with cover for ammonia refining.

emulsion in test tubes showed that both the oil and soap were soluble in petroleum ether or ethyl ether. Alcohols such as methyl, ethyl, or isopropyl were found to dissolve an appreciable amount of the ammonium soap, along with part of the oil, so they could not be used for breaking the emulsion. Acetone in small amounts broke the emulsion, but it seemed that its quantity was critical. A few drops of water hydrated the ammonium soap, which could then be separated by centrifuging.

Since the soap-oil emulsion was broken by hydrating with water, a study of the effect of different quantities of water was made. Screw press cottonseed oil having the cup loss analysis shown in Table I was hydrated with 1, 3, and 5% water and then re-refined with 13.3 g of 16° Bé caustic soda solution per 100 g of oil. Results are shown in Table II. Water percentage of 1 to 3% was found best to hydrate the soap as a firm, solid mass. Semisolid foots resulted with 5% water.

Solubility of Ammonium Soap in Cottonseed Oil. In order to determine the efficiency of soap separation, it was necessary to determine the solubility of the soap in the oil under different conditions. Samples were prepared as follows:

Sample 1: Refined cottonseed oil to which 3% oleic acid had been added was treated with gaseous ammonia for 15 min under a pressure of 8 psig. After 2 hr standing, a top layer of clear oil separated which

TABLE I

Cup-Loss Analysis of Screw Press Cottonseed Oil

Percent free fatty acids		= 3.3%
Lye: 16° Bé	13.3 gm/100 gm oil	
Refining loss		= 9.6%
Refined color		= 3.8
Soapstock	dark and firm	

TABLE II

Hydration of Ammonium Soaps

Water used for hydrating ammonium soap, % by weight	Properties of ammonium soapstock	Ammonia refining loss, %	Caustic refining loss, %	Total refining loss, %	Refined color
1	Brown and firm	4.7	2.97	7.67	12
3	Brown and firm	5.7	2.30	8.00	12
5	Semi-solid	8 [a]	....	....	....

[a] High refining loss as a result of difficult separation of the semisolid soapstock from the treated oil.

TABLE III

Solubility of Ammonium Soap in Cottonseed Oil

Sample number	Description of sample	Percent soap by weight
1	Refined oil saturated with soap	0.59 [a]
2	Crude oil saturated with soap	1.72 [a]
3	Sample 2 heated to 140F	1.42
4	Sample 2 washed with 2% water	0.316
5	Sample 4 washed with 2% water	0.021

[a] The higher figure for crude oil is believed to be due to the presence of phosphatides.

was saturated with soap. This top layer was used as the sample.

Sample 2: Crude cottonseed screw pressed oil containing 3% free fatty acids was handled as for Sample 1.

Sample 3: Crude oil, after ammonia treatment, was heated in a water bath at 140F for 15 min, then centrifuged. Again the sample was collected from the top layer.

Sample 4: Crude oil, after ammonia treatment, was washed with 2% water, centrifuged, and sample collected from the separated oil.

Sample 5: The washed oil from Sample 4 was washed again with 2% water, centrifuged, and sample collected from the re-washed oil.

The ammonium soap in each of these samples was determined by hydrolyzing the soap to fatty acids and ammonium chloride by means of hydrochloric acid, extracting the oil and liberated fatty acids with ether, and titrating with standard alkali to determine the amount of liberated fatty acids. The original amount of ammonium soap was then calculated.

Table III shows the results for each of the samples. It can be seen that two water washes with 2% water are needed to remove the soap from the ammonia treated oil.

Solubility of Ammonia in Cottonseed Oil. The solubility of ammonia in cottonseed oil was determined by two methods:

1. *Gravimetric:* Refined cottonseed oil was mixed with different quantities of oleic acid. The concen-
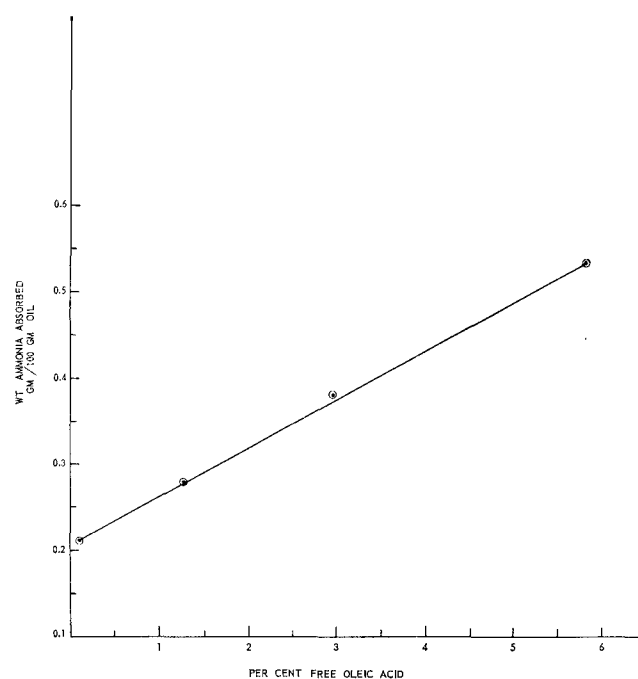

FIG. 2. Solubility of ammonia in cottonseed oil containing different quantities of free oleic acid.
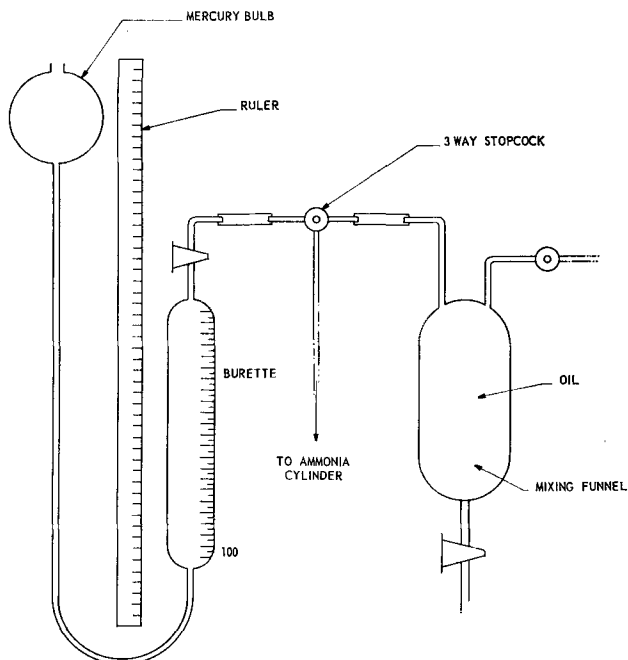
FIG. 3. Apparatus for volumetric determination of ammonia solubility in cottonseed oil.

tration of acid was checked by titration with standard alkali. The prepared samples were treated with gaseous ammonia under a pressure of 8 psig for 15 min, a period which was believed long enough for the ammonia to react with the free fatty acids and to saturate the oil. The weight of ammonia absorbed was calculated as the difference in weight of the assembly before and after adding the ammonia. The amount of ammonia absorbed by the oil samples was plotted in Figure 2 as a function of the percentage of free oleic acid. The result was a straight line which when extrapolated to 0% acid content gave 0.202 g ammonia per 100 g of oil as the solubliity of ammonia in neutral oil at 8 psig.

2. *Volumetric Method:* The apparatus for the volumetric determination of ammonia solubility in cottonseed oil is shown in Figure 3. Approximately 250 ml of refined cottonseed oil was weighed and placed in the separatory funnel leaving an empty space of 110 ml. The burette was then filled with ammonia through the 3-way stopcock. The difference in the mercury level in the burette and the bulb was read on the ruler to determine the pressure. The ammonia
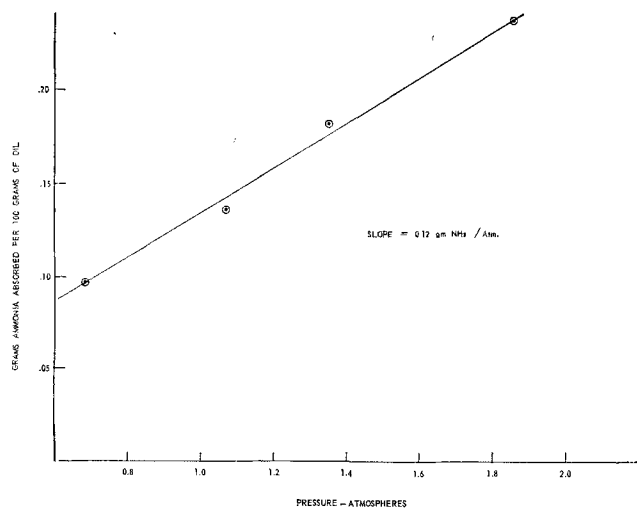

FIG. 4. Solubility of ammonia in cottonseed oil.

TABLE IV
Re-refining Screw Press Cottonseed Oil with Different Concentrations of Caustic Soda Solution

Ammonia refining loss, %	Caustic soda solutions		Caustic refining loss, %	Total refining loss, %	Refined color
	Concentration ° Bé	Quantity, %			
5.2	16	5	2.3	7.5	12.0
5.2	20	4	2.75	7.95	13.3
5.3	20	6	3.50	8.8	9.0
....	10 a	10.8	....	....	27.3
....	12 a	8.8	....	....	14.5

a The last two runs were made to determine the effect of lower concentrations on color removal.

was then passed to the separatory funnel where it was thoroughly mixed with the oil. This process was repeated with more ammonia until the oil became saturated and the mercury level in the burette reached equilibrium. The final pressure was calculated from the difference in mercury level at the end of each run. The final pressure was changed by raising or lowering the mercury bulb at the beginning of the run.

The weight of ammonia absorbed by the oil was calculated from the volume absorbed by the general gas law. Figure 4 shows a plot of the results. The best straight line between the plotted results has a slope of 0.12 g of ammonia per atmosphere. At 8 psig, the weight of ammonia absorbed is .206 g per 100 g of oil, which agrees well with the 0.202 g obtained by Method 1.

Ammonia Refining of Cottonseed Oil. Since ammonia is a weak alkali and does not attack the color bodies in cottonseed oil, the refining with ammonia should be followed by caustic refining for the purpose of color removal.

Screw press cottonseed oil was treated for 15 min with ammonia at 8 psig. The step was followed by two water washings with 2% water by weight of the oil, centrifuging and separating. The refining loss was calculated by two methods, the difference between weight of oil before and after treatment and the difference between weight of soapstock and weight of ammonia absorbed plus weight of water used for washing. If the results did not agree within 0.5%, the test was re-run.

The oil was re-refined with caustic soda solutions of different concentrations. The re-refining was done by stirring the specified amount of caustic and the oil with a high speed (3600 rpm) stirrer for 5 min. The oil was then centrifuged and separated. The refining loss was determined as before and the refined color was determined photometrically (12).

Table I gives the cup loss analysis of the screw press cottonseed oil used in these tests. The ammonia refining test results are given in Table IV. The 20° Bé caustic soda solution gave the best refined color and the 16° Bé had a lower refining loss. The refining losses were lower than for cup refining but the colors were much higher.

Ammonia Refining of Cottonseed Oil Miscella. Four cottonseed oil miscellas were prepared having 94, 74, 43, and 23% oil in hexane. The cup loss analysis of the solvent extracted cottonseed oil used in these experiments is given in Table V. The extract was first concentrated by evaporation under vacuum and then

TABLE V
Cup-Loss Analysis of Solvent-Extracted Cottonseed Oil Used in Ammonia Refining of Miscellas

Percent free fatty acids		= 1.0%
Lye: 14° Bé	6.2 gm/100 gm oil	
Refining loss		= 4.9%
Refined color		= 3.4
Soapstock	dark and fine	

TABLE VI
Ammonia Refining of Cottonseed Oil-Hexane Miscella

	O_1	O_2	O_3	O_4
Percent refining loss due to caustic re-refining				
C_1Q_1	0.94	1.53	1.09	1.31
C_1Q_2	1.08	1.92	1.01	2.45
C_2Q_1	3.83	2.03	2.22	3.05
C_2Q_2	2.43	2.15	1.94	3.32
Percent total refining loss				
C_1Q_1	4.91	5.34	3.73	3.31
C_1Q_2	5.04	5.73	3.65	4.45
C_2Q_1	7.80	5.84	4.85	5.05
C_2Q_2	6.40	5.96	4.78	5.32
Refined color of re-refined oil				
C_1Q_1	10.3	6.0	(145)	(145)
C_1Q_2	9.4	5.8	(130)	(145)
C_2Q_1	40.5	78.6	(145)	(145)
C_2Q_2	52.0	86.0	(145)	(145)

$O_1 = 94\%$ oil in miscella.
$O_2 = 74\%$ oil in miscella.
$O_3 = 43\%$ oil in miscella.
$O_4 = 23\%$ oil in miscella.
$C_1Q_1 = 20°$ Bé caustic soda solution 2.5%.
$C_1Q_2 = 20°$ Bé caustic soda solution 5.0%.
$C_2Q_1 = 36°$ Bé caustic soda solution 1.2%.
$C_2Q_2 = 36°$ Bé caustic soda solution 2.4%.

diluted to concentration used. Each miscella was treated with ammonia gas at 8 psig for 15 min and the ammonium soapstock was separated by twice washing with water. The water used each time was 2% of the weight of the oil in the miscella. It was thoroughly mixed with a stirrer for 5 min. The refining loss due to this ammonia treatment varied with miscella concentration as follows: 94%–R.L. = 4.0, 74%–R.L. = 3.8, 43%–R.L. = 2.6, and 23%–R.L. = 2.0.

Samples of the ammonia refined miscellas were re-refined with 20° Bé and 36° Bé sodium hydroxide solutions. Two different quantities of each concentration were used for each of the four miscellas. The re-refined samples were clarified by stirring for 2 min with 0.2% by weight of Filter-Cel, AOCS St'd., and filtering. The solvent was evaporated under vacuum and color of the oils determined photometrically.

The experimental values obtained are given in Table VI. These results were analyzed statistically. For refining losses due to the caustic re-refining step, the oil concentration in the miscellas was non-significant; only the concentration of the caustic was significant. The 20° Bé caustic solution produced less refining loss than the 36° Bé caustic solution.

For total refining loss both oil concentration and caustic concentration were important. This meant that the ammonia pretreatment of miscellas of lower oil concentration resulted in lower refining losses as previously noted. Both oil concentration and caustic concentration had a highly significant effect on refined color. The quantity of caustic solution did not. A 20° Bé solution removed the color for 74% and 94% miscellas. A 36° Bé caustic only removed the color for 94% miscellas and then partially.

Ammonium Hydroxide Refining of Cottonseed Oil Miscellas. For comparative purposes, the 94, 74, and 43% miscellas prepared for ammonia refining were also refined with the theoretical amount of 14.7% ammonium hydroxide solution and with a 20% excess of theoretical. The ammonium hydroxide treatment was followed by one water wash with 2% water. Re-refining with 2.5% of 20° Bé caustic was conducted as

TABLE VII

Treatment	Refining loss			Refined color		
	94%	74%	43%	94%	74%	43%
Ammonia	4.9	5.3	3.7	10.3	6.0	145
Theoretical ammonium hydroxide	7.0	5.7	2.9	8.0	8.0	Very high
20% Excess theoretical ammonium hydroxide	8.2	6.6	3.3	6.8	6.6	Very high
	Cup loss = 4.9%			Ref. color = 3.4		

previously shown under ammonia refining. Table VII lists the results along with corresponding results for the ammonia treatment.

Better results were obtained by the gaseous ammonia treatment than by the ammonium hydroxide. Neither was as good as the standard cup procedure.

Degumming of Cottonseed Oil Miscellas. Cottonseed oil-hexane miscellas containing 94, 74, and 43% oil were degummed with distilled water, gaseous ammonia, ammonium hydroxide solution, formic acid, and acetic acid under similar conditions. The phosphorous content of the crude oil and the degummed, de-solventized samples was determined by a colorimetric method (13). The percent phosphatides removed in each case was then calculated as a measure of the degumming efficiency. The quantities, concentrations, and procedures were as follows:

Water: Two washes with 2% water, stirring for 5 min each time.

Ammonia: Mixing with gaseous ammonia for 15 min under a pressure of 8 psig. followed by two 5 min water washes using 2% water each time.

Ammonium Hydroxide: Mixing with the theoretical amount of 14.7% of ammonium hydroxide solution to react with the free fatty acids followed by one 2% water wash.

Formic Acid: Mixing with 1% of concentrated formic acid followed by two 2% water washes.

Acetic Acid: Mixing with 1% of glacial acid followed by two 2% water washes.

Each treatment was followed by centrifugation and separation. The percentage of phosphatides removed is given in Figure 5. The phosphatide removal is higher at higher miscella concentrations. Gaseous ammonia is more efficient than the other reagents tested. It removed 91.6% of the phosphatides from the 94% miscella and 83.3% from the 74% miscella. All of the electrolytes gave better results than water degumming.
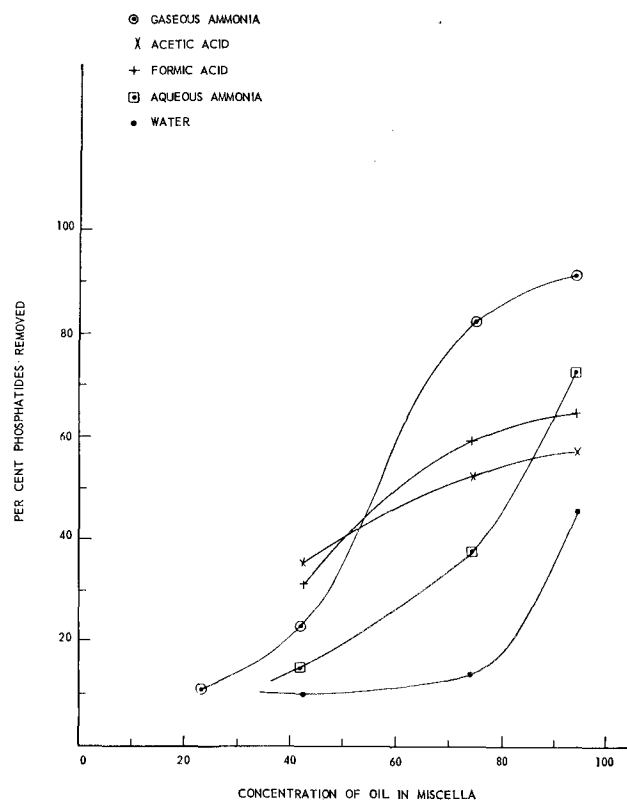

⊚ GASEOUS AMMONIA
✗ ACETIC ACID
+ FORMIC ACID
⊡ AQUEOUS AMMONIA
● WATER

FIG. 5. Degumming of cottonseed oil miscellas.

Summary

This study was an exploratory one to survey the possibilities of ammonia for refining. Persons familiar with cottonseed oil refining recognize that techniques with respect to temperature, concentration, stirring rates, and the like, have an enormous influence on results. It is believed from this study that gaseous ammonia refining could be developed to equal or surpass present "two-step" processes. "Two-step" processes used for cottonseed oil refining all suffer from the need to re-refine with strong caustic to remove color. If an alternate color removal step is ever developed, gaseous ammonia refining might become a leading process. It is one of the least expensive raw materials. Furthermore, the ammonia could be recovered as such or sold as by-product ammonium sulfate resulting from acidulation of ammonium soapstocks.

REFERENCES
1. Sikes, J. K., JAOCS 34, 72-75 (1957.
2. Mattikow, M., Oil and Soap 19, 83-87 (1942).
3. Tyler, L. D., Food Inds. 20, 1456-59 (1948).
4. Rosenstein, L., and W. J. Hund. Can. Pat. No. 327,357 (1932).
5. Van Dijick, J. D., U. S. Pat. No. 2,268,786 (1941).
6. Clayton, B., U. S. Pat. No. 2,686,794 (1954).
7. Clayton, B., U. S. Pat. No. 2,769,827 (1956).
8. Clayton, B., U. S. Pat. No. 2,374,924 (1945).
9. Frankel, E. E., Chemical Engineering 60, 356-7 (1953).
10. Thurman, B. H., JAOCS 30, 493-6 (1953).
11. Altschul, A. M., M. L. Koran, L. Kyame, M. Caravella, Oil and Soap 20, 258-62 (1943).
12. AOCS Official and Tentative Methods.
13. Harris, W. D., and P. V. Popat, JAOCS 31, 124-27 (1954).

Iron Sequestration by Polyphosphates

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Abstract

The equilibrium sequestration of ferric and ferrous iron by polyphosphates has been measured at room temperature in the pH range of 4-11. In general, sequestration decreases with increase in pH or increase in the chain length of the polyphosphate. The dissociation constants of ferric pyrophosphate and ferric tripolyphosphate have been estimated to be around 10^{-23}. The polyphosphates form weaker ferrous complexes.

Introduction

SEQUESTRATION is the formation of soluble complexes of metal ions in the presence of other chemicals that would normally precipitate the metal ion. The chemicals that are capable of interacting with metal ions in this fashion are known as sequestering agents or sequestrants.

Sodium polyphosphates are the most widely used commercial sequestrants. In previous articles (3-5) the sequestration of calcium and magnesium by the polyphosphates was quantified. This article includes information on ferrous and ferric complexing by sodium polyphosphates, as well as an estimation of the dissociation constants of the complexes formed. Previous work in this area has been sketchy and has combined sequestration with the ability of polyphosphates to peptize iron hydroxide precipitates.

Experimental Procedure

Materials. Since commercial polyphosphates differ in composition, only purified and well-defined materials were used in this study. Crystalline tetrasodium pyrophosphate decahydrate and pentasodium tripolyphosphate hexahydrate (7) were used as sources for $Na_4P_2O_7$ and $Na_5P_3O_{10}$, respectively. The three anhydrous long chain sodium polyphosphates were characterized by their Na_2O/P_2O_5 ratios of 1.34, 1.15, and 1.033, indicating along with end-group titrations average chain lengths of 6, 14, and 60 phosphorus atoms per molecule, respectively. Other chemicals were C.P. grade.

Procedure. The developed procedure was found to be applicable to ferrous as well as ferric sequestration measurements. An aliquot volume of acidic iron chloride solution containing 2.5% iron was pipetted into a beaker and about 150 cc of distilled water was added along with aqueous sodium hydroxide to give the desired pH. The slurry was agitated for 20 min prior to addition of an aliquot of 2.5% stock sodium polyphosphate solution. After further pH adjustment, the solution was shaken on a wrist-action shaker for 48 hr to reach equilibrium. To coagulate colloidal iron hydroxides, the equilibrated mixture was centrifuged for 90 min at 23,000 g's in a Lourde centrifuge, refrigerated to maintain the temperature at 25 $\pm$ 1C. The supernatant solution was filtered and an aliquot was taken for iron determination. With ferrous iron, de-aerated water was used throughout to prohibit excessive oxidation.

Iron Determination. It was found that X-ray fluorescence is a convenient and precise method to measure either ferrous or ferric iron concentration. A single measurement took only a few minutes and was accurate to $\pm$ 5 ppm iron. A Phillips Norelco X-ray spectrograph was standardized beforehand using 5 ml aliquots of stock iron solutions. The response of the instrument in the concentration range of up to 1500 ppm iron was independent of the oxidation state of iron or the presence of phosphate in solution. A tungsten target tube and a lithium fluoride crystal were used for the determination with a flow proportional detector. The analysis line was the iron K-alpha with a wave length of 1.94 Å. The calibration curve, corrected for water background counts, followed the straight line equation

$$\text{ppm iron} = 0.112 \, y$$

up to an iron concentration of 800 ppm, where y is the observed count per second. For the few determinations above 800 ppm, the iron concentration was read directly from the calibration curve.

A few initial ferric determinations were made iodometrically. The results agreed well with the X-ray values.

To make sure that only a negligible amount of the ferrous iron was oxidized to ferric during equilibration, a representative number of analyses were checked by oxidation-reduction titrations, using ceric sulfate and Ferroin indicator. No significant oxidation was detected.