

OTHER TYPES OF CRACKING TESTS

With the advent of fluid catalyst cracking other tests employing powdered catalyst have been developed and are also being used. These more recent test methods have the advantage that pilling is not required and that short catalyst holding times may be more easily studied. On the other hand, some difficulty has been experienced in testing powders of widely differing particle size. In such cases it is difficult to adjust for the effect of particle size on gas-to-solid contacting and hence on the conversion (activity index) obtained.

In general it may be said that the fixed-bed test method described in this paper does not give results of high precision, but it has been extremely useful and has contributed a great deal to the development of catalytic cracking. The emphasis has been on rapidity in order to survey a broad and extensive field. The need

for improved precision for a more intensive study of certain factors has become a prime consideration in the continuing development of cracking test methods.

LITERATURE CITED

- (1) Brunauer, S., Emmett, P. H., and Teller, E., *J. Am. Chem. Soc.*, **60**, 309 (1938).
- (2) Carlsmith, L. E., and Johnson, F. B., *IND. ENG. CHEM.*, **37**, 451-5 (1945).
- (3) Murphree, E. V., Brown, C. L., Fischer, H. G. M., Gohr, E. J., and Sweeney, W. J., *Ibid.*, **35**, 768-73 (1943).
- (4) Murphree, E. V., Gohr, E. J., and Brown, C. L., *Ibid.*, **31**, 1083 (1939).
- (5) Voorhies, Alexis, Jr., *Ibid.*, **37**, 318-22 (1945).

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Composition of Rosin Size Precipitate

OCCURRENCE OF ALUMINA

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A method for determining alumina in wet rosin size precipitate floc has been developed and applied. Its use showed that a standardized size precipitate contained no appreciable amount of alumina; this demonstrated that the aluminum ion, rather than alumina, was necessary for the formation of an effective rosin size precipitate. It was also shown that any excess alkali introduced into the papermaking system reacted with alum to form alumina, which coprecipitated with the rosin size.

MANY conflicting opinions exist at the present time both in the theory and in the practice of papermaking. One unanswered question of importance in this field concerns the roles of alumina [hydrated Al_2O_3 or $\text{Al}(\text{OH})_3$] and the aluminum ion in the formation and performance of an effective size precipitate. An outline of the literature concerning alumina in the sizing system was prepared and briefly discussed by Collins, Davis, and Rowland (4) in 1941. To obtain a general view of the present status of opinion, recent conclusions will be listed briefly. Collins *et al.* (4), from their study of ranges of complete precipitation of alumina and/or rosin, favor the view that the rosin size precipitate is a coprecipitate of alumina and rosin rather than a precipitate of a compound such as aluminum resinate; this seems also to be the view of Booth (3). Miller (11) and Redd (15), on the other hand, have concluded that the aluminum ion, rather than alumina, is necessary for the formation of an effective size precipitate. Miller and Booth both advocate the use of more, rather than less, alum than is current practice in papermaking; Price and Cameron (12), in order to improve sizing, advise reducing the amount of alum used in many cases. [Papermakers' alum, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, is designated as alum throughout the paper.]

The present work shows that alumina, as $\text{Al}(\text{OH})_3$, is not a part of a standardized size precipitate (defined in a later section), and that it is therefore the aluminum ion rather than alumina which is necessary for the formation of an effective rosin size precipitate.

This paper represents a portion of a broad program, now in progress, designed to study the physical and chemical phenomena involved in rosin sizing of paper.

ANALYSIS FOR ALUMINA

The first step toward determining the role of alumina in the sizing mechanism consists of developing a method of analyzing the size precipitate for alumina. With such an analytical tool it is then possible to determine whether alumina, as such, is a necessary component of the size precipitate, whether it occurs during some sizing operations, and under what conditions it appears.

An analytical method for determining alumina in size precipitate flocs has been developed and is fully described in a later section. A standardized procedure of preparing the precipitate from rosin size and alum was used to obtain a standardized size precipitate for analysis.

Of greatest importance to the fundamental knowledge of rosin sizing is the fact that the alumina determination showed the absence of alumina in such a standardized size precipitate. Figure 1 shows typical potentiometric curves. While the standardized size precipitate (curve II) required more acid to reach pH 3.5 than did the distilled water adjusted to pH 4.5 with alum (curve I), the form of its curve is quite distinct from that obtained with an alumina suspension (curve III). In contrast to the rapid fall of pH with the addition of acid found for the standardized size precipitate, the alumina suspensions maintained their pH above 4 until practically all the floc had reacted with the acid. The pH then dropped comparatively rapidly; the point of inflection was located at about pH 3.5. Hence Figure 1 illustrates the absence of alumina, as such, in standardized size precipitate.

Curve II of Figure 1 is typical in form not only of emulsions of size A (70% solids, 20% free rosin) but also of solutions of size B (a dry neutral size), and was found whenever the precipitate was prepared in distilled water. Moreover, distilled water, adjusted to pH 4.5 with alum, contained no floc and showed no alumina by electron microscope examination. Since satisfactory sizing can be obtained with these sizes on a neutral pulp with distilled water used as the papermaking water (14), it follows both from the analyses and the papermaking that alumina [$\text{Al}(\text{OH})_3$] is not a component of standardized size precipitate.

Data to be presented show that sodium carbonate, sodium bicarbonate, and sodium hydroxide added to the size reacted, apparently quantitatively, to form alumina when the size was

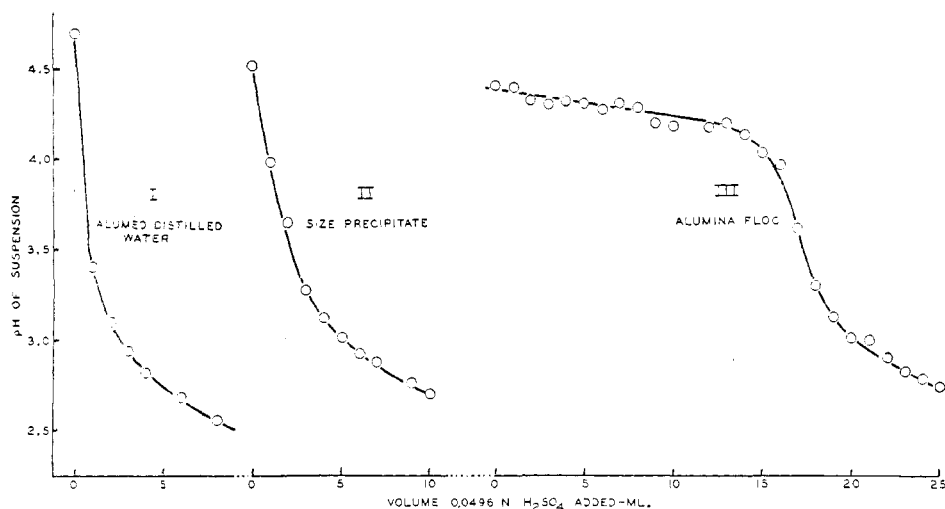


Figure 1. Comparison of Potentiometric Curves for Standardized Size Precipitate and for Alumina

treated with alum to a final pH of 4.5. Hence, it is obvious that excess alkali introduced in the water or in the pulp will cause the formation of alumina, which will coprecipitate with the normal size precipitate.

Another series of precipitates investigated were those made in sodium and calcium bicarbonate waters. They were chosen to parallel conditions of the paper sizing study described in a previous paper (12).

Former work on sizing in bicarbonate waters showed that the best sizing was achieved at a pulp slurry pH of about 6.5. Accordingly, precipitates were made in tap water, adjusted to pH 7.0 with sulfuric acid, to which 12.5 ml. of 6.05% sodium carbonate and, in some cases, 4.95 ml. of 10% calcium chloride were added per liter. Throughout this discussion alkaline hard waters refer to a bicarbonate ion concentration equivalent to 450 parts per million of calcium carbonate. Generally an equivalent amount of Ca^{++} ion was also present; the results were the same whether Ca^{++} ion was present or not. After this water was adjusted to pH 6.5 with sulfuric acid, 25 ml. of 3% size A was added per liter, and alum was added to the mixture to obtain a pH of 4.5. The possible change in the tap water composition from day to day was considered the most important uncontrolled variable in this procedure. That this was not generally serious can be seen in the reproducibility of results on different preparations shown in Table I. Three results of the eighteen determinations seem to be obviously in error: they have been omitted from the average. The rest of the data showed an acid requirement of 11.8 ml. of 0.0516 N sulfuric acid; the maximum variation from this value was 5%. Hence, size precipitate made under these conditions contained $21.0 \pm 1.0\%$ $\text{Al}(\text{OH})_3$ based on the size or $17.4 \pm 0.9\%$ based on

the total precipitate. This amount of alumina in papers made in the presence of other alkalies was definitely detrimental to sizing (14). The sizing improvement obtained from a pulp slurry pH of 6.5 which was observed for treated bicarbonate waters must, therefore, be due to some other factor.

A determination of alumina in size precipitate from calcium bicarbonate hard waters with adjusted pH (3.0 to 8.0) was also made; this corresponds to conditions studied by papermaking in a previous paper (12). The results are given in Table II and plotted in Figure 2. In order to apply the data from the wet suspension to comput-

ing percentage composition of the precipitate, the alumina has been regarded as $\text{Al}(\text{OH})_3$ or $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. The percentages computed on this assumption are plotted (Figure 2) against the pH of the water in which the corresponding precipitates were made. This shows no correlation with the analogous sizing curve of the preceding paper (13) for bicarbonate waters.

CONCLUSIONS. (a) A method of analysis for alumina in rosin size precipitate has been developed. (b) Use of this method showed that standardized size precipitates contain no alumina. (c) Alkali introduced into the papermaking system by water or pulp will react with alum to form alumina which will be coprecipitated with the alum-size precipitate.

DETERMINATION OF ALUMINA

Present opinions of the composition of rosin size precipitate and, therefore, of the roles of alumina and of aluminum ion in sizing are confused because no satisfactory analytical methods have been available for the determination of alumina, aluminum resins, and free resin acids, as such, in the precipitate which is formed. [Methods reported in the literature for the study of the composition of the precipitate consisted of determinations of total ash and of solvent extractions (16). Later work will consider the effect of the presence of cellulose on the size precipitate composition. The existence of such an effect has been emphasized in Bialkowsky's work (2) which preceded more recent studies of base exchange capacity of cellulosic material.] The first effort made in this work to determine alumina, as such, in the presence of aluminum resins and of resin acids was by x-ray studies. Various size precipitates, prepared at beater concentrations of size and of alum were vacuum dried and examined. They were all amorphous, although some exhibited a halo at 5.8 \AA . A sample of alumina was then prepared by adding alum to a 0.0133% sodium carbonate solution to a pH of 4.5. (This solution is equivalent in concentration to 3.0% size based on pulp of 2.5% consistency.) The precipitate was filtered off, washed free of sulfate (barium chloride test) with 0.01 M ammonium hydroxide, and dried in a vacuum desiccator. This alumina sample was completely amorphous by x-ray examination and showed only one faint line by electron diffraction. It seems quite likely, therefore, that any alumina present in size precipitate will be amorphous and not detectable by these physical means. Refractive indices were equally ineffective for this analysis.

DEVELOPMENT OF TITRATION METHOD. The difficulties of quantitative titration of aluminum salts with alkalies are well known (6). Some of the difficulties are introduced by the heterogeneity of the reaction mixture and by the characteristic surface

TABLE I. ALUMINA IN SIZE PRECIPITATES FROM BICARBONATE WATER OF pH 6.5 AND BICARBONATE CONTENT EQUIVALENT TO 450 P.P.M. CaCO_3

Ppts. in Order of Prepn.	0.0516 N H_2SO_4 Required by 100-Ml. Ppt. Suspension, Ml.	Ppts. in Order of Prepn.	0.0516 N H_2SO_4 Required by 100-Ml. Ppt. Suspension, Ml.
1	11.9	9	11.8
2	(13.5) ^a	10	11.6
3	(13.8) ^a	10	11.8
4	11.7	10	11.3
5	(10.7) ^a	10	11.4
6	11.6	11	11.7
7	12.0	11	12.0
8	11.5	12	12.1
9	11.9	13	12.4
		Average	11.8

^a Values in parentheses omitted from average.

properties of the alumina formed. For a titration of alumina with acid, however, the end point would occur with a homogeneous system. It was therefore decided to attempt a titration of dilute alumina suspensions with dilute standard acids. After each addition of acid the mixture was stirred until the pH was constant; this meant 2 hours in some cases and days in others. A rapid titration was impossible and would give meaningless curves, since the reaction was not complete until an appreciable time after the acid had been added.

Alumina suspensions were prepared by adding alum to an ammonia solution of pH 10 to obtain a pH of 4.5. Standardized size precipitates were prepared by adding 25 ml. of 3% size A (70% total solids, 20% free rosin) to a liter of distilled water and adding alum to pH 4.5. A 100-ml. sample of suspension was used for the titrations, and 0.05 N acid was added in 1-ml. portions. The suspension was stirred vigorously throughout the determination, and the steady pH was recorded when it was attained after each acid addition. Not only was the reaction slow, but attainment of equilibrium of the glass electrodes of the Beckman industrial-model pH meter with the suspension required an appreciable length of time; occasionally the electrodes had to be cleaned with acid. Consequently, the curves of Figure 3 portray determinations which extended over a period of days.

Curves III and IV of Figure 3 show that the alumina suspensions maintained their pH above 4 until practically all of the floc had reacted with the acid. The pH then dropped comparatively rapidly; pH 3.5 seemed to be the point of inflection. These curves are quite different from those reported by Datta (5) for alumina sols. His curves showed nothing corresponding to the point of inflection at pH 3.5. All the titrations of Figure 3 were carried out with 0.05 N sulfuric acid, except for curve IV in which hydrochloric acid was used. Although curve V shows, for a suspension of the amorphous alumina prepared for x-ray examination, a behavior very similar to suspensions in which the alumina has not been dried, subsequent preparations of dried alumina exhibited insolubilized portions of the material. Hence, these determinations have been applied only to wet flocs and to those of less than two weeks' age.

In contrast to the curves of alumina, curve I is the control, a titration of distilled water adjusted with alum to pH 4.5. Curve II is for a standard size precipitate; while it required more acid to reach pH 3.5 than did the control, the form of its curve is quite distinct from that of the alumina curve. Curve VI shows that an artificial mixture of 50% alumina suspension and 50% size precipitate suspension required slightly more than half the acid demanded by an equal amount of alumina suspension. This would be expected from the acid requirements shown by curve II

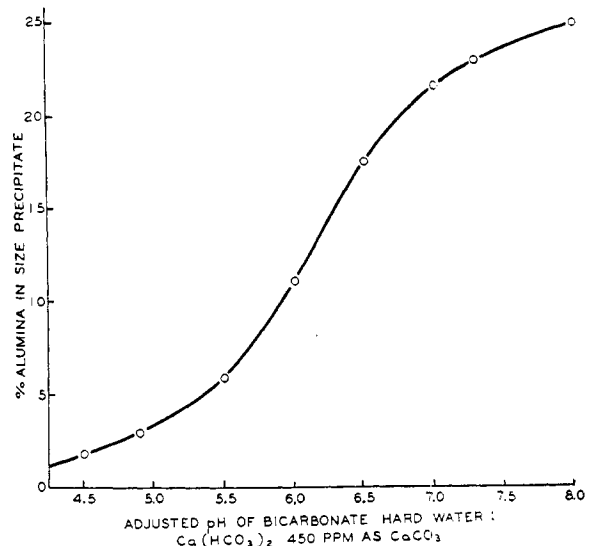


Figure 2. Alumina Formed in Size Precipitates in Alkaline Hard Water

(size precipitate); and by curve III (alumina). Curve VII for a soft tap water adjusted with alum to pH 4.5 shows that this procedure detected small amounts of alumina. Finally, curve VIII illustrates the fact that, when size precipitate was prepared in alkaline water, all of the excess alkali reacted with alum to form alumina, which, in such cases, was coprecipitated with the size. There seems no doubt that this procedure offers a method of determining the relative amount of alumina present in a given size precipitate mixture.

REVISED METHOD. Because these determinations were so tedious, and because of the possibility of errors being introduced during the lengthy procedure, a revision was made to allow greater speed and accuracy. As before, a 100-ml. sample of the dilute alumina suspension was used. An excess of 0.05 N acid, generally 25 ml., was added to this. If the approximate amount of alumina is unknown, the excess of acid must be determined. Any amount of acid which produces a solution of pH less than 3.5 after reaction is adequate. In general, an excess to give pH 2.5 or less was used. The mixture was allowed to stand overnight, although a shorter time may be used in most cases, and then back-titrated to pH 3.5 with 0.05 N sodium hydroxide. The equivalence of the two methods may be illustrated by the following typical determinations on 100-ml. portions of the same alumina suspension at pH 4.5:

TABLE II. ALUMINA IN SIZE PRECIPITATES MADE IN ALKALINE HARD WATER OF 450 P.P.M. $\text{Ca}(\text{HCO}_3)_2$ AS CaCO_3

pH of Water Adjusted with H_2SO_4^a	0.0516 N H_2SO_4 Used by 100-ml. Size Ppt. Suspension, ml.	0.0516 N H_2SO_4 Required by Alumina in Size Ppt. Suspension, ml.	$\text{Al}(\text{OH})_3$ 0.75 G. Size, G.	$\text{Al}(\text{OH})_3$ in Total Size Ppt., %	Al from $\text{Al}(\text{OH})_3$ in Total Size Ppt., %
3.0	0 ^b	0	0
4.5	4.65	1.05	0.0138	1.81	0.63
4.9	5.32	1.72	0.0227	2.94	1.02
5.0	1.19 ^b
5.5	7.14	3.54	0.0466	5.85	2.03
6.0	10.65	7.05	0.0928	11.00	3.80
6.5	16.60	12.00	0.158	17.4	6.02
7.0	19.23	15.63	0.206	21.5	7.44
7.3	20.48	16.88	0.222	22.8	7.88
7.5	8.15 ^b
8.0	22.03	18.43	0.248	24.8	8.58
Control (standardized size ppt.)	3.60	0.0	...	0	0

^a This adjustment frees CO_2 which is not immediately lost from system; hence adjusted waters are not at equilibrium when used.

^b Interpolated.

Original Revised Method Method

Vol. 0.0494 N H_2SO_4 to attain pH 3.5, ml. 19.5 19.4
Vol. control (100 ml. distilled water plus alum, pH 4.5), ml. 0.5 1.0
Vol. acid required by alumina present, ml. 19.0 18.4
Time required by determination, days 19 0.67

The two methods, therefore, agreed within about 3.0%, and much of this difference could have been introduced by extraneous factors such as laboratory fumes, rinsing of electrodes, etc., which would affect the 19-day determination. Hence, the revised method was used for the rest of the work. [This revised method is similar to a procedure used by Graham (7) in the analysis of hydrous alumina sols. It differs in the nature of the starting material and in the end point of the back-titration. However, the principle is the same in both cases.]

As had been indicated in the preliminary work, the relative amount of alumina in prepared mixtures of alumina and size precipitate suspensions could readily be found. For such determinations the control used was the standardized size precipitate at pH 4.5 rather than distilled water alumed to pH 4.5. As indicated in Figure 3, the size precipitate consumed, probably by hydrolysis, some of the acid which was added.

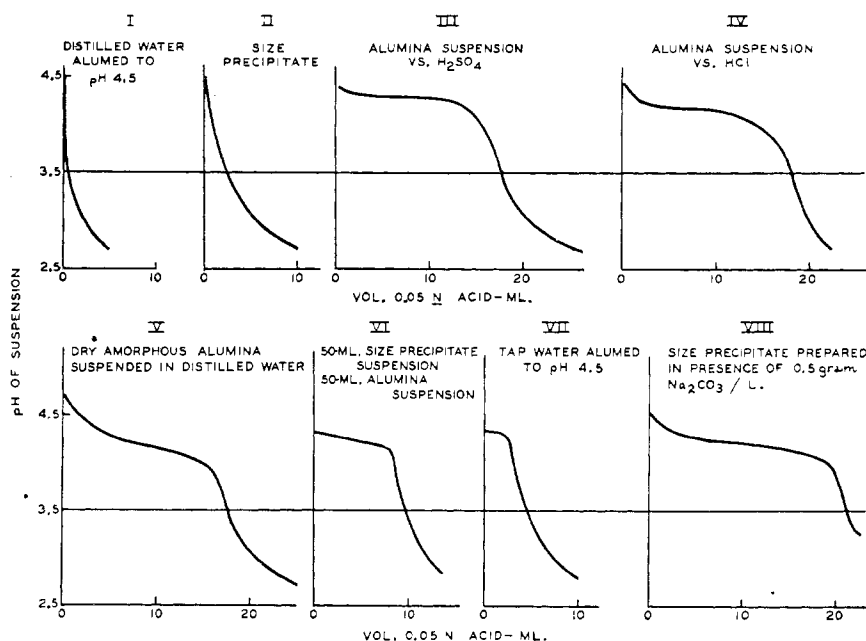


Figure 3. Potentiometric Curves for Various Suspensions

CHEMICAL FORM OF ALUMINA

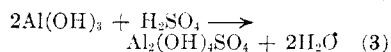
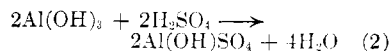
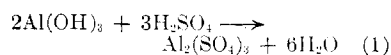
Although the method just described offers a fairly convenient way of determining relative amounts of alumina present, the absolute quantity cannot be determined until the chemical form of the alumina, and its reaction with acids, is known. Mellor (10) lists a multitude of basic aluminum salts which various investigators have reported; both soluble and insoluble sulfates are included. Miller (11) believes that the alumina floc at pH 5.4 is the basic salt $5\text{Al}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 4\text{H}_2\text{O}$, and that $\text{Al}(\text{OH})_3$ is formed only at pH 8.7. Weiser *et al.* (19) report an insoluble product of the approximate composition $\text{Al}_2\text{O}_3 \cdot \text{SO}_3 \cdot 1.5\text{H}_2\text{O}$ which loses no SO_3 at 600°C . and decomposes at 700°C . This material was obtained from aluminum sulfate solutions at pH < 5.5 and gave an x-ray diffraction pattern different from that of $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. However, Imhoff and Burkhardt (8) could not identify the alumina in flocs at pH 4.5 as a basic salt. Alumina prepared at pH 4.5 for this work and examined by x-ray was either amorphous (one sample) or gave the pattern for boehmite, $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (several samples). Therefore, the floc at pH 4.5 was considered to be essentially $\text{Al}(\text{OH})_3$. It is realized, of course, that the aluminum ion is highly hydrated, and that a variety of physicochemical changes occur in the course of aging the floc (18). No study was made of this aspect of the subject, but its probable influence was recognized by the specifications given here for the preparation and age of the suspensions.

If $\text{Al}(\text{OH})_3$ is the skeletal formula for the initial material, then it reacts with sulfuric acid to form $\text{Al}_2(\text{SO}_4)_3$ or some soluble basic sulfate at pH 3.5. Mellor (10) mentions several such sulfates, and Wilson (20) has patented the preparation of $\text{Al}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 9\text{H}_2\text{O}$. When the titration (preliminary method) of the alumina suspension was stopped at pH 3.5 and the solutes were recovered by evaporating this solution, the solid material was amorphous to x-ray examination. After standing for 10 days, the material gave a faint x-ray diffraction pattern; after heating to 370° or 430°C ., its x-ray pattern was definite but did not correspond to any in Hanawalt's catalog (1). When the material was heated to 550°C ., the x-ray pattern was that of anhydrous $\text{Al}_2(\text{SO}_4)_3$. A sample of Merck's c.p. $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ showed the x-ray pattern reported by Hanawalt for this hydrate. Upon heating to 200°C ., the material became amorphous. Further heating to 430°C . converted it to anhydrous $\text{Al}_2(\text{SO}_4)_3$. The x-ray evidence is, there-

fore, inconclusive as to the product of the reaction; the intermediate pattern might be that of a basic sulfate or of a hydrate other than the common one of $\text{Al}_2(\text{SO}_4)_3$. Many other hydrates have been mentioned, but their x-ray patterns are not available.

An indirect method of determining the reaction product is through the acid requirement of a definite amount of alumina.

Thus:



are some possible reactions if the basic sulfates shown are soluble. However, the acid requirements are distinctly different, and all samples titrated indicate that the reaction is according to Equation 1 (Table III).

Another indirect method of establishing the reaction product was used.

To determine the amount of alumina present in dilute suspensions as accurately as possible, 1-liter samples of the suspension were used instead of 100-ml. samples. The first suspension was prepared by adding alum to tap water to pH 4.5. A control was prepared by adjusting the pH of tap water to 4.5 with sulfuric acid. The 1-liter samples were first run in duplicate by the revised method. The data obtained were:

Sample	0.0512 N H_2SO_4 Required, ml./liter
Alumina floc suspension 1	33.24
	33.26
Average	33.25
Control	7.89
	7.91
Average	7.90

One liter of this alumina suspension, therefore, required 25.35 ml. of 0.0512 N sulfuric acid to dissolve the floc. If the reaction results in the formation of the normal $\text{Al}_2(\text{SO}_4)_3$, this amount of acid is equivalent to 11.7 mg. per liter of aluminum in the floc as alumina.

Samples of this same suspension and of its clear supernatant liquor were acidified and analyzed for total aluminum content by the haematoxylin method (17). The determination gave:

Sample	Total Al (Haematoxylin Method), Mg./liter
Alumina floc suspension 1	31, 31
Supernatant liquor	20, 20
Difference, Al in floc	11

By these analyses, the aluminum in the alumina floc amounts to 11 mg. per liter. This is an excellent agreement with the 11.7 mg. per liter found by acid titration, on the assumption of the formation of $\text{Al}_2(\text{SO}_4)_3$, in view of the limitations of the colorimetric analysis.

SUMMARY OF METHOD

X-ray work has shown that the alumina from a floc at pH 4.5 is aluminum hydroxide rather than a basic sulfate. (The x-ray evidence of boehmite and, therefore, of $\text{Al}(\text{OH})_3$ as the initial

TABLE III. ANALYSIS FOR ALUMINA ON VARIOUS FLOCS

Alkali Used to Prepare Alumina at pH 4.5	Alkali/Liter Milliequivalent Required by Equation 1 ^a	H ₂ SO ₄ Required to Dissolve Alumina, Milliequivalent/Liter	Milliequivalent Required by Equation 2 ^a	Size Present
Na ₂ CO ₃	29.8 ^b	30.0 ^c	19.7	Yes
NaHCO ₃	9.5 ^d	9.7 ^d	6.3	No
NaOH	6.8 ^b	6.9 ^d	4.5	No
NaOH	3.2 ^b	3.1 ^d	2.1	Yes
NaOH	6.9 ^b	6.9 ^d	4.6	Yes
NaOH	12.1 ^b	12.3 ^d	8.0	Yes

^a Equations: (1) $2\text{Al}(\text{OH})_3 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Al}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O}$; (2) $2\text{Al}(\text{OH})_3 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{Al}(\text{OH})\text{SO}_4 + 4\text{H}_2\text{O}$.

^b By titration of alkali with standard acid.

^c By titration of suspension with 0.05 N H₂SO₄, original method.

^d By titration of solution or suspension with 0.05 N H₂SO₄, revised method.

material does not rule out the possible presence of basic salts amorphous to x-ray examination, in which $\text{Al}(\text{OH})_3$ is present as a unit in a larger structure. For example, Kohlschütter (9) proposes a basic salt of the composition $\text{AlCl}_3 \cdot 2\text{Al}(\text{OH})_3$. Acid would attack such a structure with the removal of the alumina, and the presence of the normal salt would have no effect on the titration. However, the analytical determination of $\text{Al}(\text{OH})_3$ as a chemical unit is attained whether the initial material is in the complex or the simple form.) When such a floc has reacted with sulfuric acid and therefore obtained a pH of 3.5, the product in solution is the normal aluminum sulfate. On this basis the revised method of determining alumina in dilute suspensions and in the presence of size precipitate gives the absolute amount of alumina in the sample. It may be used on fresh (aged not more than 2 weeks) wet precipitates (pH 4.5), and consists of adding a known amount of 0.05 N sulfuric acid (in excess of amount required by the alumina present) to the sample, allowing 16 hours for complete reaction, and back titrating to pH 3.5 with 0.05 N sodium hydroxide standardized against the standard sulfuric acid. The presence of materials other than size and alumina does not interfere unless such materials form a complex with alumina or show buffering action between the pH values 4.5 and 3.5. With the

proper volume sample and the use of proper controls the amount of $\text{Al}(\text{OH})_3$ may be determined as equivalent to the acid used—that is, formation of normal salt—to within 5% or better of the amount of size precipitate used in this investigation.

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LITERATURE CITED

- (1) Am. Soc. for Testing Materials and Am. Soc. for X-Ray and Diffraction, Card Index of X-Ray Diffraction Data, original set and 1st supplement.
- (2) Bialkowsky, H. W., *Paper Trade J.*, **97**, No. 13, 29-46 (1933).
- (3) Booth, L. M., *Ibid.*, **106**, No. 8, 122-4 (1938).
- (4) Collins, T. T., Jr., Davis, H. L., and Rowland, B. W., *Ibid.*, **113**, No. 13, 94-9 (1941).
- (5) Datta, N. P., *J. Indian Chem. Soc.*, **19**, No. 5, 191-203 (1942).
- (6) Davis, H. L., and Farnham, E. C., *J. Phys. Chem.*, **36**, 1057-74 (1932).
- (7) Graham, R. P., dissertation, Columbia Univ., 1942.
- (8) Imhoff, C. E., and Burkhardt, L. A., *IND. ENG. CHEM.*, **35**, 873-82 (1943).
- (9) Kohlschütter, H. W., *Kolloid-Z.*, **96**, 237-44 (1941).
- (10) Mellor, J. W., "Treatise on Inorganic Chemistry," Vol. V, New York, Longmans, Green & Co., Inc., 1942.
- (11) Miller, L. B., *Paper Trade J.*, **108**, No. 2, 34-40 (1939).
- (12) Price, D., and Cameron, D. D., *Pulp Paper Mag. Can.*, **40**, No. 3, 142-8 (1946).
- (13) *Ibid.*, **40**, No. 3, 142-8, Figure 2 (1946).
- (14) Price, D., and Cameron, D. D., unpublished work.
- (15) Redd, J. C., *Paper Trade J.*, **119**, No. 7, 42-7 (1944).
- (16) Robinson, J. J., *Ibid.*, **103**, No. 7, 104-12 (1936).
- (17) Strafford, N., and Wyatt, P. F., *Analyst*, **68**, 319-24 (1943).
- (18) Thomas, A. W., and Whitehead, T. H., *J. Phys. Chem.*, **35**, 27-47 (1931).
- (19) Weiser, H. B., Milligan, W. O., and Purcell, W. R., *IND. ENG. CHEM.*, **33**, 669-72 (1941).
- (20) Wilson, W. S., U. S. Patent 2,323,499 (July 6, 1943).

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Molal Refractions of Mononuclear Aromatic Hydrocarbons

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The molal refractions of mononuclear aromatic hydrocarbons are additive in a homologous series, and may be expressed by an equation of the form $R = k + an$, where R is molal refraction, calculated by either the Lorenz-Lorentz formula or the Gladstone-Dale formula, and n is the number of carbon atoms. Constants a and k have been evaluated by the method of least squares for fourteen homologous series of mononuclear aromatic hydrocarbons.

A RECENT collation and critical evaluation of data on physical constants (3) has made readily available all recorded values for density and refractive index of mononuclear aromatic hydrocarbons. These data have been used to evaluate the effect of structure on molal refraction, which is both an additive and a constitutional property. It cannot be predicted, therefore, unless the effects of structure are known. Molal refraction depends on refractive index, density, and molecular weight. For com-

parative studies molal refraction is preferred to refractive index because of the minimization of effects of temperature and density.

Molal refractions of aliphatic hydrocarbons for the sodium D line are additive within a single homologous series. For many series of aliphatic hydrocarbons the effect of adding a CH_2 group is constant (13). The effects of structure, such as increments in molal refraction caused by branching and by unsaturation, have been thoroughly investigated and evaluated for aliphatic hydrocarbons (7, 8, 13).

Physical constant data for aromatic compounds are not nearly so complete as those for the aliphatics. They are, however, sufficient to permit evaluation of the relation between molal refraction and the number of carbon atoms for fourteen homologous series of mononuclear aromatic hydrocarbons.

CALCULATIONS

Molal refractions have different numerical values, depending on how they are defined. The different systems are internally