A FEW REMARKS ABOUT BASIC SULPHATE OF ALUMINA.[1]

BY W. C. FERGUSON.

MANY samples of commercial sulphate of alumina contain more or less of an excess of alumina over that required to form the normal sulphate ($Al_2(SO_4)_3$), the amount varying from a trace to 2½ per cent. and occasionally even more.

The following composition is of frequent occurrence:

Total soluble alumina = 17.00 per cent.; soluble alumina calculated from sulphuric anhydrate (SO_3) to form $Al_2(SO_4)_3$ = 15.2 per cent., leaving 1.8 per cent. of alumina in excess of that required to form the normal sulphate.

It is concerning the probable chemical constitution of this alumina in excess of that required to form the normal sulphate, together with its behavior towards resin soap in the manufacture of paper, that this brief article is written.

As is well known, in sizing paper sulphate of alumina is made to react on resin soap (made by saturating soda ash with resin), thus precipitating an insoluble alumina soap, a resinate of alumina in the fiber of the paper.

In many paper works the per cent. of normal sulphate $Al_2(SO_4)_3$ determines the strength of the material bought and, other things being favorable, that is preferred which contains the highest per cent. of $Al_2(SO_4)_3$.

A number of reports from paper mills are about as follows:

$$\begin{cases} \text{Combined } Al_2O_3 = 15.20 = Al_2(SO_4)_3 = 50.96 \\ \text{Free } Al_2O_3 \qquad = 1.80, \text{ or} \end{cases}$$

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In such reports the "combined" Al_2O_3 and also the $Al_2(SO_4)_3$ are calculated from the SO_3 present and the soluble so-called "free" Al_2O_3 is ignored as being of no value for sizing purposes. This idea that has so little, if anything, to support it, is discussed below.

A solution of normal sulphate of alumina behaves very much

[1] Read January 12, 1894.

like an acid; it combines with bases, evolves hydrogen with metals, and is acid to litmus paper. We should, therefore, expect SO_3 to combine with more alumina than is represented by the normal sulphate, and it might be added that as weak bases have the characteristic of forming basic salts, we should for this reason also anticipate the formation of basic sulphates of alumina. These basic sulphates can readily be formed in the laboratory from the normal sulphate.

1. By dissolving alumina in the normal sulphate.

2. By action of caustic alkalies on a solution of the normal sulphate. $Al_2(SO_4)_3 + Na_2O = Al_2O_3(SO_3)_2 + Na_2SO_4$.

For example: A solution of normal sulphate of alumina containing seven per cent. of alumina can be made two per cent. basic by adding caustic soda slowly to a hot solution until a precipitate forms that does not dissolve even on long boiling. This is equivalent in a seventeen per cent. material to having 4.86 per cent. in excess of that required to form $Al_2(SO_4)_3$.

3. By action of a metal, $Al_2(SO_4)_3 + Zn + H_2O = ZnSO_4 + Al_2O_3(SO_3)_2 + H_2$.

These equations are only intended to illustrate the probable types of reaction; it is not assumed that just such compounds are formed.

The following standard works treat of a number of basic sulphates of alumina that are soluble in water:

"Watts' Dictionary of Chemistry,"
"Roscoe & Schorlemmer's Chemistry,"
"Mendelejeff's Principles of Chemistry."

A careful search through the literature fails to reveal any reference to "free" alumina existing in a solution of normal sulphate.

The term "free" implies the reverse of combined and from the considerations given above it is not deemed best to call the alumina contents in excess of that required to form normal sulphate "free," with every condition favoring combination. Such alumina is undoubtedly combined as basic sulphate and being in solution there is every reason to believe that it would form a resinate of alumina with resin soap as readily as the normal sulphate, and some ground for the assumption that it might be even more available because it is probably held in weaker combination and so would be more readily decomposed and precipitated as size; and if this were true such basic alumina would be more valuable than the normal because more would be precipitated by a given weight of resin soap. With these considerations in mind the following investigations were carried out in the laboratory. In order to observe the action of resin soap on a solution in which the alumina approaches nearest to the free state some aluminate of soda was prepared by dissolving alumina in caustic soda. In this solution alumina is so feebly held in combination that the weakest acids, such as carbonic, will replace it. The solution is basic, and alkaline to test paper.

Resin soap immediately precipitates a voluminous precipitate of resinate of alumina. Even upon the addition of a drop or two of resin soap the precipitate begins to form.

A comparison of a neutral sulphate containing seventeen per cent. soluble alumina and of a basic sulphate containing seventeen per cent. total soluble alumina, fifteen per cent. being normal and two per cent. being basic, the so-called "free," were each treated with an equal amount of resin soap in such quantity that but a portion of the alumina was precipitated. The solutions were filtered and precipitates washed with equal amounts of water and ignited. It was found that under such conditions

4.40 grams were precipitated from the neutral solution,
6.98 grams were precipitated from the basic solution.

These results are what theory would anticipate.

A brief summary of the case is this: It would seem that there is no "free" soluble alumina in the basic sulphate of alumina of commerce; such alumina is in direct combination as basic sulphate and being more feebly held in combination than alumina combined as normal sulphate, more readily forms size with resin soap and is therefore more economical, less resin soap being required for a given weight of sulphate. It directly follows from this that in any sulphate of alumina the $Al_2(SO_4)_3$ should be calculated from the total soluble alumina and *not* from that combined as normal sulphate alone, as in the latter case the most valuable alumina content is ignored as being useless. The following example will serve to illustrate the difference in value based on the two types of analyses: In a sulphate of alumina analyzing

Total soluble alumina	17.00	per cent.
Alumina combined as normal	15.20	" "
Basic alumina = so-called "free"	1.80	" "

The $Al_2(SO_4)_3$ calculated from 15.20 per cent. of alumina equals 50.96 per cent., whereas if calculated from 17.00 per cent. the $Al_2(SO_4)_3$ equals 57.00 per cent. In conjunction with these figures it must be borne in mind that experiment proves the basic sulphate of alumina to be relatively even more efficient than the difference in the above interpretations of analysis indicate.

DROPPING FLASK FOR STANDARD SOLUTIONS.[1]

By Frank Vanderpoel.

It is well known that in working with standard solutions, the strength of the latter, when determined by the volume used, is influenced by the temperature to quite an appreciable extent. In fact, if a solution be standardized at 25° C. and afterward used at 20° C., its strength at the latter temperature is 1.001 times what it was at the former. For this reason it is necessary when employing volumetric apparatus to note the temperature of the solutions if very accurate work be done.

Again it has been observed that burettes and delivery pipettes sometimes vary in the volume of liquid delivered, this variation depending upon the nature of the solution or the ease with which it wets the sides of the glass tube, as all solutions are not the same in this respect.

With an apparatus so made, however, that the standard solution is weighed instead of measured, these objections disappear, while accuracy is not impaired; in fact, with a common balance, sensitive to one centigram, much finer work can be done by weighing the solution than by measuring with a burette which reads to tenths of a cubic centimeter.

A number of dropping flasks and bottles have been invented from time to time with the above object in view; the one here represented having been devised some four or five years ago and kept in constant use in my laboratory ever since. It is quite simple and consists of a cylindrical or globular flask provided with two openings at the top and a dropping tube at the bottom

[1] Read December 8, 1893.