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A MODIFIED METHOD FOR DETERMINATION OF THE COPPER NUMBER OF PAPER

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method described in this paper 30 minutes was found to give quite consistent results which did not vary greatly by longer treatment. Reduction of the test specimen to a finely divided condition is considered essential in reducing the time of treatment and producing complete reaction.

The method is particularly adapted to testing high-grade rag-fiber bond papers. Such papers are usually internally sized with rosin, surface sized with animal glue and pressed very hard in the finishing process. Owing to their hardness and toughness they are very resistant to the usual procedure employed for this determination but very accurate test results are obtained by the modifications described.

II. PREPARATION OF THE PAPER SAMPLE

In testing high-grade rag-fiber bond papers, because of the heavy glue surface sizing and the hard finish, it was found impossible to obtain accurate results which could be duplicated when a sheet of the paper was used or even if the paper were cut into very small fragments, although in the latter case much more uniform results were secured than in the former case. Uniform and accurate results were obtained only when the paper specimens were finely ground. The paper when ground had the appearance of finely cut cotton and was extremely well adapted to chemical treatment and washing. While such treatment may not be necessary in the case of soft, weak papers it is believed that grinding of the paper for this determination should be made standard procedure. In fact, such preparation of the paper is highly desirable for most chemical tests of paper which depend on extraction of the paper by liquid solvents, as paper fibers hold absorbed substances tenaciously.

The grinder used for this purpose was constructed similar to one used at the Swedish Government Testing Institute by Gösta Hall⁵ and was designed by him. It consists of a 12-inch rotor fitted with six serrated steel lugs, which revolves inside a steel housing, the inner surface of which is also serrated around its circumference. The rotor teeth clear the stator teeth by a sixteenth of an inch. The rotor is driven at the rate of 1,700 revolutions per minute which gives the rotor teeth a speed of a little over a mile per minute. The dry paper is introduced in the form of strips through a slot and enters the rotor space near the center whence it is carried by centrifugal force into the space between the rotor teeth and the stator teeth. It is there disintegrated by impact and is ejected through a 7-mesh screen into a receiver in the base of the apparatus. Disintegration in this manner does not heat the paper, a consideration of much importance.

⁵ "Acidity in paper," by S. Köhler, in charge of paper section, Government Testing Institute, Stockholm, Sweden, and G. Hall, chemist, Albemarle Paper Manufacturing Co., Richmond, Va.; *The Paper Industry*, 7, No. 7; October, 1925.

The advantage of using ground-paper samples instead of cut pieces is easily demonstrated by the molybdate method of titration. It is nearly impossible to remove all of the blue color of molybdenum from cut pieces, especially if the paper is heavily sized, whereas this washing process is accomplished with ease on the ground paper. The failure to remove all of the blue molybdenum in the washing process is a source of error which reduces the copper number. The blue color of the molybdenum is so intense as to afford a very good indication as to when the sample has been washed sufficiently, and for this reason is to be preferred to the iron solution commonly used.

III. PREPARATION OF THE SOLUTION

1. COPPER SULPHATE (FEHLING SOLUTION A)

To 4 liters of distilled water are added 277.3 g of copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and the mixture is shaken at intervals until the copper sulphate has gone into solution. The copper sulphate should be of high purity and as free from iron as possible.

2. ALKALINE TARTRATE (FEHLING SOLUTION B)

One hundred and fifty grams of sodium hydroxide of good quality and 500 g of sodium potassium tartrate are dissolved in 1,500 ml of distilled water.

3. FEHLING SOLUTION

Fehling solution is prepared by the careful addition of the copper sulphate solution (A) to an equal amount of the alkaline tartrate solution (B). It may be kept ready mixed, but should in this case be carefully protected from air and light, as it is apt to undergo changes which render its indications unreliable. Before using a mixed solution which has stood for some time, a small amount should be diluted and heated to boiling for a few minutes. A perfectly clear solution indicates that the solution is still satisfactory for use. It is, however, preferable to keep the two solutions separate until they are needed.

4. MOLYBDOPHOSPHORIC SOLUTION

Dissolve 100 g of sodium molybdate (43 per cent Mo) and 75 ml of phosphoric acid (83 per cent) in a solution containing 275 ml concentrated sulphuric acid and 1,750 ml of distilled water.

5. POTASSIUM PERMANGANATE SOLUTION

Dissolve 6.25 g of potassium permanganate in 1 liter of distilled water, filter through an asbestos mat in a Gooch crucible, and dilute to a total volume of 4 liters.

IV. STANDARDIZATION OF THE SOLUTION

The standardization is done according to the directions given in circular No. 40 of the Bureau of Standards,⁶ with certain modifications due to the difference in the strength of the potassium permanganate solution. In a 400 ml beaker dissolve 1.5 to 2.0 g of sodium oxalate in 150 to 200 ml of hot water, 80° to 90° C., and add to this solution 6.5 ml of sulphuric acid (1 : 1). Titrate at once with the permanganate solution, stirring the liquid vigorously and continuously. The permanganate solution must be added slowly, not more than 10 to 15 ml per minute, and the last 0.5 to 1.0 ml must be added drop by drop with particular care to allow each drop to be fully decolorized before the next is added. The temperature of the solution at the end should not be below 60° C.

V. PROCEDURE

Determinations are always carried out in duplicate and if possible in triplicate, the final figure being an average of these separate values.

One and a half grams of the ground-paper sample are added to a solution of the following composition, after a temperature of 100° C. has been reached: 25 ml of copper sulphate solution, 25 ml of tartrate solution, and 125 ml of hot distilled water. This mixture is heated with gentle stirring in a 500 ml wide-mouth Erlenmeyer flask in a water bath containing 30 per cent calcium chloride. The temperature of this bath is maintained at about 110 to 115° C. so as to keep the liquid in the flask at a gentle boil during the time it is being treated. The temperature of the copper solution should not go below 100° C. during the period of treatment, which should be approximately 30 minutes.

The solution is then filtered while hot on a 5.5 cm filter paper⁷ in a Büchner funnel and washed with 250 ml of hot water. The paper fiber and the filter paper are then transferred to a 250 ml beaker and 25 ml of the molybdate solution added. After allowing the mixture to stand for a short time 25 ml of water are added and the mixture stirred so as to disintegrate the filter paper. The solution is then filtered as before and washed with about 200 ml of cold water. This washing must be done thoroughly so as to remove all of the blue molybdenum color.

The blue solution is now titrated with the standard permanganate solution until a permanent pink is obtained. The titration can be carried out accurately without danger of adding an excess of permanganate since the blue solution changes to colorless just before it goes to pink and thus gives a definite warning of the approaching end point.

⁶ Government Printing Office, Washington, D. C., 5 cents each.

⁷ A No. 40 Whatman filter paper gave good results.

VI. CALCULATION OF RESULTS

The copper number of the sample is determined by multiplying the number of milliliters of potassium permanganate used in the molybdenum titration by the calculated factor and dividing the result by the number of grams of sample used. The copper number may thus be defined as the number of centigrams of metallic copper in the cuprous oxide reduced from the cupric sulphate by 1 g of sample. The factor, which is dependent on the exact titer of the potassium permanganate solution, is the number of centigrams of copper, in the cuprous oxide, equivalent in reducing power to the oxidizing power of 1 ml of the potassium permanganate solution.

For example, the factor of a potassium permanganate solution is 0.2714; that is, 1 ml $\text{KMnO}_4 = 0.2714$ cg Cu. In an analysis, using 1.5 g of sample, 5 ml of potassium permanganate solution are required in the titration. The copper number of the sample is calculated as follows:

$$\frac{\text{mlKMnO}_4 \times \text{factor}}{\text{Grams of sample}} = \frac{5.0 \times 0.2714}{1.5} = 0.9046$$

or the copper number of the sample.

WASHINGTON, June 18, 1927.