The apparatus functions practically as a large-scale Soxhlet extractor with constant instead of intermittent syphon. For extractors it has been found very convenient to use 3-gal. copper fire extinguishers.

The apparatus described in this article has been found very useful for other continuous extractions with organic solvents when it is desired to treat several kilograms of material.

METHOD OF PREPARING PHLOROGLUCINOL REAGENT FOR THE KREIS TEST

By Henry W. Dixon

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The Kreis¹ test has been found to be a useful chemical test for the detection and estimation of rancidity in fats when considered together with the taste, odor, and flavor. If a supply of phloroglucinol is not available, the Kreis reagent may be conveniently prepared by the following method, based on Barth and Schreder's synthesis of phloroglucinol from resorcinol.²

Dissolve 100 g. of sodium hydroxide in 40 cc. of water by heating slowly in an iron or nickel container. Cool to a temperature at which a few crystals of resorcinol dropped into the liquid do not become brown, and stir in 15 g. of resorcinol. Cover with a watch glass to exclude air and at the same time to permit observation, and heat for 2 or 3 hrs. in a sand bath until the melt is a dark chocolate-brown. (If the melt is heated too fast or too long, charring will take place with low yield of phloroglucinol. If the reaction is not carried to completion, unchanged resorcinol will interfere with the color of the Kreis test.) Cool, still excluding air. Dissolve the melt in about 500 cc. of water, heating gently if necessary. Transfer to a beaker, cool in ice and cautiously add concentrated hydrochloric acid until the solution is acid. Extract repeatedly by shaking with 100 cc. portions of ether in a separatory funnel. Combine the ether extracts and bleach by shaking with animal charcoal. The filtered ether extract should be kept as a stock solution. To prepare the Kreis reagent dilute a portion of the stock solution with ether until it gives a good reaction with a strongly rancid fat but a less intense reaction on further dilution.

Fifteen grams of resorcinol ordinarily yield 10 l. or more of the Kreis reagent. This reagent appears to be a satisfactory substitute for that prepared from pure phloroglucinol.

A COLLOIDAL METHOD FOR INCREASING THE VOLUME OF ADHESIVE WATER-GLASS

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Commercial silicate of soda, or water-glass, with a density of about 42° Bé., is used in very large quantities as an adhesive in the fiber container industry.

¹ Kerr, This Journal, 10 (1918), 471. 2 Ber., 12, 503.

In fact, this material is the only adhesive employed for gluing together the components of both doublefaced corrugated board and laminated solid fiber board.

During a recent emergency created by freight embargoes and other war-time causes of delay, the stocks of water-glass in the box-makers' hands began to run low. This laboratory was at that time confronted with the problem of increasing the volume of the 42° Bé. adhesive without injuring its essential properties. These properties, which make water-glass of especial value to the box-board industry, may be classed as follows:

(1) Adhesive value. (A powerful adhesive is not required, but it must be equal to or greater than the "felted" strength of the paper fibers.) (2) Proper viscosity.

 (a) Proper viscosity. (This will be discussed below.)
 (b) Low penetration. (This prevents loss of adhesive through absorption by the relatively porous corrugated strawboard. This property obviously depends upon the viscosity.)

(4) Fast setting and drying rate. (The boards are run through the pasting machines at a speed of upwards of 60 ft. per min.) (5) Relative insolubility when dry.
(6) Relative flexibility when dry.
(7) Negligible effect of age.
(7) This is the second of the second sec

(7) Negligible effect of a(8) Relatively low cost. (This is necessary because container board is a product of relatively low cost.)

Water-glass at about 42° Bé. is a fairly viscous liquid. High viscosity is one of its desirable features for use in this industry, and is only limited by the fact that it must be fluid enough to be pumped to various parts of the factory and to flow over the troughs and rollers as fast as needed. High viscosity prevents loss by absorption and insures a satisfactory drying rate and adhesive power. Initial attempts to increase the volume of a given amount of the adhesive were made by diluting with water. This naturally lowered the viscosity to a very marked extent and the drying rate and adhesive power were correspondingly lowered to a prohibitive degree. Much of this adhesive, moreover, was absorbed by the strawboard. These experiments clearly showed that the desirable properties of water-glass as an adhesive are, in general, a function of the viscosity, and as this is lowered these properties suffer proportionately.

The problem was finally solved by diluting the water-glass with brine.¹ It was found possible by this means to increase the volume of the solution by 25 per cent without lowering the original viscosity or detracting from any of the essential qualities of the adhesive as listed above. This process was perfected on a laboratory scale and subsequently tried out on a large scale in several factories. It was found to work satisfactorily, the only disadvantages being:

(1) The possibility of a drop in the market price of water-glass.

The increased floor and storage space required. (2)

(3) The installation of equipment.

Water-glass is a complex mixture including sodium silicate (probably hydrated), water and silica (or silicic acid) in the colloidal state. The actual proportions of Na₂O and SiO₂ to form the compound Na₂O. $xSiO_2$, and the proportion of SiO_2 in the colloidal form, are questions about which much uncertainty

¹ The writer desires to acknowledge his indebtedness to Dr. E. W. Tillotson, Jr., assistant director of Mellon Institute, for his suggestions and assistance in the development of this method.

still exists. They no doubt vary in different lots of water-glass. Most investigators are of the opinion . that the silica is in chemical combination to the extent of $Na_2O_2SiO_2$ and that any excess SiO_2 over this amount is merely "dissolved." Analyses of water-glass are reported in terms of Na_2O , SiO_2 and H_2O . The adhesive grade usually contains from 3.0 to 3.5 parts of SiO_2 to one part of Na_2O .

When an electrolyte is added to water-glass the colloidal SiO_2 is coagulated. This forms what is sometimes termed a "weakly agglutinated gel" which, if undisturbed, soon coalesces to a dense mass. This, of course, is a well-known method of preparing the silicic acid gel, preparatory to dialysis.



Fig. 1-The Effect on the Viscosity of Water-Glass Produced by the Addition of Various Brines

If, however, the water-glass solution is stirred during the addition of certain electrolytes and for a short time afterwards, the gel particles do not have a chance to coalesce, but will go back into "solution," *i. e.*, they are "peptized." Fortunately, brine, a cheap and readily accessible reagent, was found to coagulate and peptize the gel in a more satisfactory manner than any of the other more or less cheap solutions experimented with. This peptization of the gel is accompanied by an enormous increase in viscosity over that which results from dilution of the waterglass with an equal volume of plain water.

This final viscosity depends upon the concentration of the added brine, other factors being constant. The volume of most water-glasses can be increased to the extent of 25 per cent by the addition of a brine about two-thirds saturated, and with no loss in viscosity, adhesive power or drying rate. Small increases in the concentration of the brine beyond this point cause proportionately greater increases in the viscosity and the final solution soon loses all fluidity. This is shown graphically in Fig. 1. Twenty parts by volume of brine were added to eighty parts by volume of four different commercial brands of water-glass. All determinations were made at 20° C. All were increased in volume by the same amount with brines of varying concentration. The effect on each sample is distinctly different, yet the analyses of the original samples are so similar that a relation between analysis and the effect of brine is not clearly indicated.¹ This is due, perhaps, to variations in the relative proportion of silica in the colloidal state and would not be indicated by the nature of the analytical method. Owing to lack of time, the samples were not dialyzed, although dialysis would probably account for this action. It will be noticed, however, that the viscosity of all four samples was lowered to the same point by the addition of an equal amount of plain water, regardless of the original viscosity.

Water-glass thickens so rapidly when exposed to the air, and moves so slowly through ordinary viscosimeters, that only "comparative viscosities" were determined. These determinations were made by measuring with a stopwatch the time required for each solution to flow past marks at the top and bottom of the same 20 cc. pipette under constant conditions. This time, in seconds, was recorded as a measure of the "relative viscosity."

It was found in each case that an increase of 25 per cent in the volume of the water-glass was the maximum efficient amount. More brine than this makes the peptization process increasingly difficult, until a concentration is soon reached which entirely inhibits this action.

In practice the adhesive user can easily plot a viscosity curve by treating small lots of his particular supply of water-glass with a set of standard brines of different concentrations. He can then determine the proper brine concentration for reaching that final viscosity which best suits his needs.

The actual treatment is made on a fairly large scale, using mechanical agitators or stirrers. The stirring does not have to be violent but merely enough to keep the liquid in motion. Agitation of a measured quantity of water-glass is started, and the corresponding volume of brine is then added to the mixture in several fine streams. If the brine is added too fast or in too coarse a stream the resulting gelatinous curds are so large that a longer time is required for peptization, due to the smaller surface area presented. When all the salt solution is added the batch has a sticky consistency, but in a few minutes begins to recover fluidity. The stirring must be continued until no more curds are present. On a small scale, 20 to 30 min. suffice, while on a large scale this may have to be increased, depending upon the rate at which

¹ In attempting to find some such relation it was noticed that when the ratio of SiO₂ to Na₂O was plotted against the concentration of brine necessary to duplicate the original viscosity, the four samples fell approximately on a straight line (Fig. 2). More data would be necessary to establish the significance of this relation. It is no doubt true, however, that as the proportion of Na₂O increases, stronger brines are necessary for reaching the original viscosity. Thus, a fifth sample having a ratio of 2: 5 (10.65 per cent Na₂O) showed approximately the same final viscosity whether treated with plain water or saturated brine. Water-glasses of comparatively low alkalinity are, on the other hand, extremely viscous even in the original state. the brine was added and upon the efficiency of the stirring operation.

The cost of this treatment is low, since the final increased adhesive only contains from 3 to 4 per cent, by weight, of NaCl. Any ordinary grade of salt seems to work satisfactorily.



The final viscosity can be varied to a large extent by small changes in the brine concentration. This is shown by the steepness of the curves in the neighborhood of the "original viscosities." This brine concentration, however, can be controlled very well in practice by the use of a standard hydrometer, since it is not at all difficult to read the latter to one-tenth of a degree, which corresponds to one-tenth of one per cent of NaCl.

The treated adhesive does not seem to be affected by age. Samples out of contact with the air have been kept and observed for over a year and show no appreciable change in adhesive power, and no loss of viscosity. After several months a flocculent sediment often settles out, but this apparently has no effect on the adhesive quality or the viscosity.¹

Samples of corrugated container board made in both laboratory and factory, with the treated adhesive, also have remained unaffected by age for a period of more than one year.

SUMMARY

I—The desirable properties of water-glass for use as an adhesive are, in general, a function of the viscosity.

II—A method is described of increasing, to the extent of 25 per cent, the volume of adhesive waterglass by the addition of brine, without impairing the viscosity and other desirable properties of the adhesive.

III—This method involves the practical application of certain phenomena of colloid chemistry, such as coagulation and peptization.

ON THE DISTILLATION OF AMMONIA

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The distillation of ammonia from an alkaline solution into standard acid and titrating or nesslerizing

¹ This same sediment is observed, to a lesser extent, when samples of ordinary water-glass are kept for some time in bottles, "and is probably due to the action of the free alkali on the glass. to determine the ammonia has long been in practice. Many procedures and forms of distilling apparatus have been suggested for transferring the ammonia into the standard acid, but all have one or more objectionable features.

A prolonged study of nitrogen methods made in connection with the biological studies of this laboratory¹ has involved the use of many different kinds of distilling apparatus. Both water- and air-cooled condensers have been used and, while many satisfactory determinations were made with air-cooled condensers, an apparatus suitable for the distillation of ammonia from an alkaline solution into standard acid should possess a water-cooled condenser. The ordinary Kjeldahl distilling rack, although water-cooled, has many undesirable features, especially when small amounts of nitrogen are being determined. The solubility of the soft glass still head and adapter ordinarily used together, with the adsorption of ammonia by the block tin condenser, led to the abandonment of this type of apparatus. The one found most satisfactory for careful research work has been described.² It is made of Pyrex glass with only one rubber connection which does not vitiate the results. The scrubbing device for removing entrained alkali is sufficiently satisfactory for use with N/100 solutions. This apparatus, however, is not entirely suited for general routine analytical work. A scrubbing device and an adapter have been devised for use with block tin condensers,³ thereby overcoming the most objectionable features of the ordinary Kjeldahl distilling rack. By using these devices with good tin condensers, proceeding as outlined below, it is easily possible to obtain an accuracy of less than I per cent with 5 mg. of nitrogen.

We desire to recommend here that the apparatus as finally adopted, *i. e.*, the all-glass apparatus or block tin condensers with the new scrubber and adapter, be used in connection with the methods described from this laboratory. While the Mitscherlich distilling apparatus was found satisfactory in this laboratory for determining nitric nitrogen, it may not prove equally so in other laboratories. The procedures for using the distilling apparatus, as recommended, in connection with the determination of nitric nitrogen and total nitrogen are given below.

PROCEDURE FOR DETERMINING NITRIC NITROGEN

The procedure⁴ previously recommended is followed with the exception of the distilling apparatus, which is replaced by that described above. The cooled condenser is used for the first 20 min. of moderate boiling, after which it is drained and the boiling continued, more rapidly, for 20 min. longer. The receiver is then removed, cooled, and titrated.

PROCEDURE FOR KJELDAHL NITROGEN DISTILLATION

The procedure followed in most laboratories consists in distilling through a water-cooled condenser until about 150° cc. of distillate have been collected.

¹ THIS JOURNAL, 7 (1915), 521; 8 (1916), 896; 10 (1918), 600; 11 (1919), 306; Ann. Mo. Bol. Gardens, 6 (1919), 1.

- ² Ann. Mo. Bot. Gardens, 6 (1919), 45.
- ⁸ THIS JOURNAL, **11** (1919), 465. ⁴ Loc. cit.

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