sented two of the paraffins of most highly centralized structure and highest aniline equivalent. Comparing paraffins and naphthenes having the same number of carbon atoms, it appears that the naphthenes lie within the range of antiknock quality that is established by the paraffins, but that on the whole the range covered by both paraffins and naphthenes seems to be approximately the same.
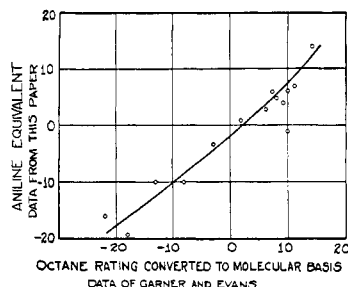
EFFECT OF UNSATURATION IN RING. The effect of the removal of hydrogen from the saturated cyclic compounds is, in general, to increase the aniline equivalent. This effect is large and the difference between the series of normal monoalkyl cyclohexanes and the corresponding cyclohexenes is about 15 units on the average. A somewhat similar situation prevails for the monoalkyl cyclopentanes and cyclopentenes.

FIGURE 3. ANILINE EQUIVALENTS vs. OCTANE RATING

For the compounds studied in the cyclohexene series, there is a considerable increase in aniline equivalent when a methyl group is added to cyclohexane although this is not true for the corresponding saturated compounds.

COMPARISON WITH OTHER DATA

The data given by Garner and Evans (3) on the knock ratings of a number of naphthenes are interesting to compare with the data given here on the same compounds. Fortunately there are fourteen compounds on which to base such a comparison.

Garner and Evans report their data in terms of the octane number of a 20 per cent solution of the hydrocarbon in a gasoline (A-2) of 50 octane number, and, in order to make a comparison, their data have been converted to a molecular basis comparable with the aniline equivalents. To do this, the increase in octane number of the fuel upon the 20 per cent addition, when measured at 212° F. jacket temperature, has been converted to a comparable molecular basis by multiplying by the factor:

$$\frac{\text{Mol. wt. of hydrocarbon} \times \text{density cyclopentane}}{\text{Mol. wt. cyclopentane} \times \text{density hydrocarbon}}$$

These computed values, which should be comparable to aniline equivalents, have been plotted against the observed aniline equivalents as shown in Figure 3. The points lie quite close to the curve as drawn, and almost all of the deviations appear not to be much greater than the probable experimental error. This excellent agreement with the valuable and thorough work of Garner and Evans is an indication of the reliability of determinations of knocking characteristics of hydrocarbons.

LITERATURE CITED

(1) Birch and Stansfield, Nature, 123, 490 (1929).
(2) Campbell, Lovell, and Boyd, IND. ENG. CHEM., 20, 1045 (1928).
(3) Garner and Evans, J. Inst. Petroleum Tech., 18, 751 (1932).
(4) Hofmann, Lang, Berlin, and Schmidt, Brennstoff-Chem., 13, 161 (1932).
(5) Lovell, Campbell, and Boyd; IND. ENG. CHEM., 23, 26 (1931).
(6) Ibid., 23, 555 (1931).
(7) Nash and Howes, Nature, 123, 276 (1929).
(8) Ricardo, Auto Eng., 11, 92 (1921).
(9) Signaigo and Cramer, to be published.

Floc Formation Studies in Water Purification

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THE importance of good coagulation in a water clarification process before sedimentation and filtration is well recognized. The writers have already discussed the importance of proper mixing and conditioning of the water with the coagulant and defined the optimum rates (8). Another important phase of good coagulation is hydrogen-ion concentration. Its relation to six of the common coagulants used in water purification are discussed here.

The use of aluminum salts, especially aluminum sulfate, as coagulants and their reactions have been the subject of many previous investigations. Hatfield (4) and Willcomb (11) summarize references and significant facts established by a number of investigators.

The different optimum pH values of coagulation, the variations in isoelectric points reported, and the conflicting opinions given by those attempting hydrogen-ion control, indicate that there are factors to consider other than pH alone. This inconsistency was studied by Peterson and Bartow (9) and Miller (6). They showed that coagulation may be retarded and confined within narrow limits by the anions present. Bartow has given additional data on this subject (2). It is generally recognized now that any attempt to establish optimum coagulation conditions must take into consideration the effect of the salts present in the water.

Therefore this value must be established for the particular water being treated.

Iron salts have been used and studied to a lesser degree in water purification than those of aluminum. Miller (7) studied the composition of iron floc using ferric sulfate and ferric chloride and working in an atmosphere of nitrogen with oxygen excluded. This work is not comparable with plant operation. Hopkins (5) made some practical studies of ferric hydroxide floc and found that when using one and two grains per gallon of $FeSO_4 \cdot 7H_2O$ the maximum turbidity removal in the waters tested occurred at pH 9.5.

At the Chain of Rocks plant of the St. Louis Water Division it had been found that with aluminum sulfate the best coagulation is obtained when the pH of the water is higher than generally recommended. This observation led to a laboratory investigation to determine the most desirable pH and to study the coagulation and relation to hydrogen-ion concentration of other coagulants. Laboratory and practical plant data with some of the coagulants used in these experiments are not recorded in the literature.

The six coagulants used are as follows:

Aluminum sulfate, the so-called crushed material, containing approximately 13.5 molecules of water.
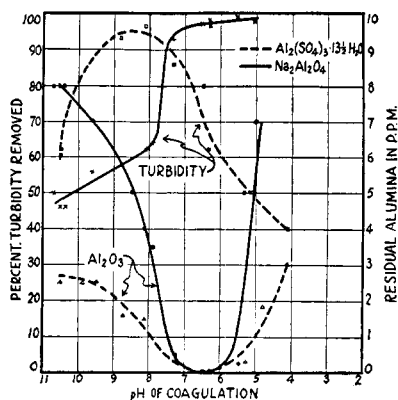
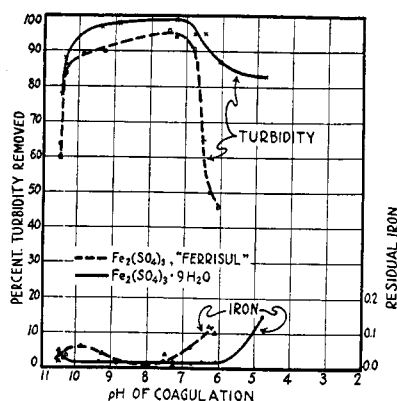FIGURE 1. COAGULATION WITH ALU-
MINUM SULFATE AND SODIUM ALUMI-
NATE

FIGURE 2. COAGULATION WITH HY-
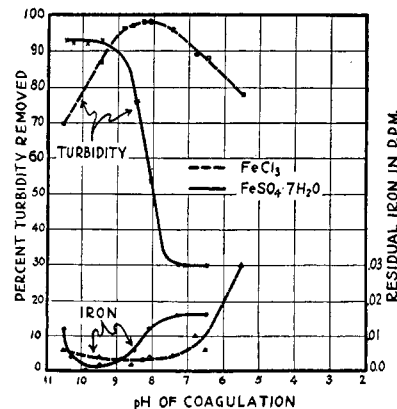DRATED FERRIC SULFATE AND FER-
RISUL

FIGURE 3. COAGULATION WITH FERRIC
CHLORIDE AND FERROUS SULFATE

Dry sodium aluminate, a commercial grade containing 85.6 per cent sodium aluminate.

Ferric sulfate, a crystalline material of technical grade which runs approximately 98 per cent $Fe_2(SO_4)_3 \cdot 9H_2O$ and 1 per cent or less ferrous sulfate.

Ferrous sulfate ($FeSO_4 \cdot 7H_2O$), used regularly at this plant and commonly known as sugar sulfate of iron.

Ferric chloride, a commercial solution testing: ferric chloride, 40.98 per cent; hydrochloric acid, 0.28 per cent; specific gravity, 1.4338.

Ferric sulfate [$Fe_2(SO_4)_3$], sold under the trade name Ferrisul, an anhydrous, grayish white powder.

EXPERIMENTAL PROCEDURE

Ten 5-gallon bottles of settled water were collected and treated with 3.5 grains per gallon of lime and allowed to settle. This water was collected from one of the settling basins at the Chain of Rocks plant. It is river water treated with lime and iron. The clear water was siphoned off and river mud was added to one bottle. Then the muddy and the clear waters were mixed to produce a turbidity of 50 p. p. m., a pH of 10.7, and a caustic alkalinity of nearly 50 p. p. m. The turbidity of the water consisted of both suspended and colloidal material. By the addition of 0.2 molar sulfuric acid and stirring for 15 minutes, this water was adjusted to the desired pH values. The charge of each of the six coagulants was one grain per gallon. All samples were stirred 30 minutes at 0.5 foot per second and allowed to settle for 30 minutes. The temperature of coagulation was kept at 22° C. (71.6° F.). The following notations and determinations were made: pH at the end of each coagulation, character of the floc and approximate time required for its formation, residual metal from the coagulant, turbidity, alkalinity, and free carbon dioxide.

Residual aluminum and iron were determined colorimetrically. The hematoxylin method outlined by Yoe (12) was used for aluminum and the method given in Standard Methods of Water Analysis (1) for iron.

ALUMINUM SALTS

The calculated percentage turbidity removed and the residual alumina using aluminum sulfate are shown in Figure 1. The minimum residual alumina was found at pH 6.5. This is near the values of 6.1 to 6.3 found by Hatfield (3) with alum upon Lake St. Clair water for the maximum rate of flocculation.

A charge of one grain per gallon of $Al_2(SO_4)_3 \cdot 13^1/_2H_2O$ is equivalent to 3.0 p. p. m. alumina. Figure 1 shows that at 97 per cent maximum turbidity removal, 50 per cent of the aluminum remained in solution. Maximum turbidity removal is not directly related to the residual aluminum, and low residual aluminum is not to be sought where turbidity removal is of first importance. There is no doubt a ratio between dissolved and suspended aluminum, and that within certain limits of this ratio flocculation is best.

The floc appeared first in the low ranges of hydrogen-ion

concentration; the particles were larger and the water appeared better coagulated than in the higher hydrogen-ion concentrations, contrary to the experience of Theriault and Clark (10) who found the most rapid and complete flocculation at pH 5.5. A distinction must be made, however, between their method and that used in the present investigation. Theriault and Clark used relatively high concentrations of aluminum sulfate in distilled water; the work described in this paper dealt with low concentrations of the coagulant in a treated natural water.

Sodium aluminate is not widely used for the treatment of municipal water supplies, probably because of its cost. The plant experiments conducted at Chain of Rocks have given unsatisfactory results from a cost standpoint and also because a coagulant is needed that will reduce the pH and convert normal carbonates into bicarbonates. In Figure 1 is shown the optimum zone of hydrogen-ion concentration for coagulation. The maximum percentage turbidity removal occurs at a lower pH than with aluminum sulfate. Here, as in the case of aluminum sulfate, the range of lowest residual does not quite match that of greatest turbidity removal.

IRON SALTS

Residual metal and comparisons between pH and turbidity removal for the iron coagulants can be made from Figures 2 and 3. In the use of ferrous salts it is important that all the iron be oxidized to the ferric state before the water reaches the filters, otherwise oxidation takes place within the filters or after the water passes through them and causes a turbid effluent water. Surface waters usually contain sufficient oxygen to accomplish this if thorough mixing and an adequate retention period are given. In some instances chlorine is necessary to complete the oxidation. Iron floc penetrates the filter bed much faster and deeper than does alum floc. After a certain length of time peptization of the floc starts producing turbidity and high residual iron in the effluent. This is avoided if the filters are washed after a certain number of hours, rather than by waiting until an 8-foot loss of head is reached. In subsequent experiments it is anticipated that more will be learned of the disintegration of iron floc. The curves for the iron salts show that the minimum range of residual iron closely matches the maximum range of the turbidity removal, but not exactly.

SUMMARY

In regard to turbidity removal, aluminum and iron salts compare favorably in their optimum ranges of hydrogen-ion

concentration. Lower residual metal is found from the iron salts than from those of aluminum.

The optimum pH of coagulation with aluminum sulfate is higher than with sodium aluminate. Of the two aluminum salts, aluminum sulfate is preferred at this plant because of its lower cost and higher pH range of optimum turbidity removal.

All the iron salts show low residual iron in the optimum range of coagulation. The two ferric sulfates have almost identical optimum pH ranges. Ferrous sulfate and ferric chloride have narrow ranges of optimum removal of turbidity, the first in water that is caustic or nearly so, and the second in water that is nearly neutral to phenolphthalein. The ferric sulfates cover wider pH ranges of greatest removal of turbidity than do ferrous sulfate and ferric chloride. Low residual metal is not a measure of the efficiency of the coagulant in removing turbidity.

LITERATURE CITED

(1) Am. Water Works Assoc., Standard Methods of Water Analysis, 7th ed., 1933.
(2) Bartow, E., paper presented before the Mo. Valley Sect., Am. Water Works Assoc., Sioux City, Iowa, Oct. 25, 1932.
(3) Hatfield, W. D., *J. Am. Water Works Assoc.*, **11**, 554 (1924).
(4) *Ibid.*, **14**, 442 (1925).
(5) Hopkins, E. S., IND. ENG. CHEM., **21**, 58–60 (1929).
(6) Miller, L. B., *Pub. Health Rept.*, **40**, 351 (1925).
(7) *Ibid.*, **40**, 1413 (1925).
(8) Nolte, A. G., and Kramer, W. A., paper presented before the Mo. Valley Sect., Am. Water Works Assoc., Sioux City, Iowa, Oct. 25, 1932.
(9) Peterson, B. H., and Bartow, E., IND. ENG. CHEM., **20**, 51–55 (1928).
(10) Theriault, E. J., and Clark, W. M., *Pub. Health Rept.*, **38**, 181 (1923); Reprint 813.
(11) Willcomb, G. E., *J. Am. Water Works Assoc.*, **24**, 1416 (1932).
(12) Yoe, J. H., "Photometric Chemical Analysis," Vol. I, Wiley, 1928.

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# Soluble Anhydrite as a Desiccating Agent

II. Drying of Organic Liquids

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THE removal of water from organic liquids is a perennial problem both in the laboratory and in manufacturing operations. None of the known desiccants and no single method have been shown to be applicable to the complete drying of any considerable number of liquids of varying properties. For the drying of any particular liquid it is usually necessary to select a particular drying agent and/or a particular method, and it is not unusual to have a drying problem arise for which none of the known desiccants and no established method are entirely suited.

The present paper describes several methods for the application of the new desiccant to the complete and rapid drying of such a variety of liquids as ethyl alcohol, ether, acetone, ethyl acetate, methyl alcohol, N-butyl alcohol, acetic acid, formic acid, pyridine, etc.

In Part I of this series (*3*) it has been shown that anhydrous calcium sulfate, prepared in either powdered or granular form by dehydration of the dihydrate or half-hydrate at temperatures below about 300° C., and commonly known as soluble anhydrite, is an efficient desiccating agent for solids and gases because of the avidity with which it takes up water vapor to revert to the half-hydrate;

$$CaSO_4 + \tfrac{1}{2}H_2O \longrightarrow CaSO_4 \cdot \tfrac{1}{2}H_2O + 2700 \text{ cal.}$$
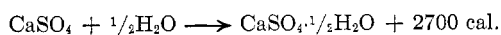
and it was suggested (*3*) that this reaction takes place in the presence of organic liquids with the effect of extracting water from them.

The inactivity of calcium sulfate toward, as well as its insolubility in, the ordinary organic liquids is well known. These fortunate properties are not altered by the processes employed in the preparation of the anhydrous salt in the

The effectiveness of a new drying agent, anhydrous calcium sulfate in the form of soluble anhydrite, for the complete and rapid drying of organic liquids is described. The high affinity of this reagent for water present in large or small proportions in organic liquids, its insolubility in and inactivity toward these liquids, its neutral reaction, its physical and chemical stability, the ease of economy of preparation and repeated regeneration, and the wide range of its applications are pointed out. It is believed that this material has proved more versatile than any drying agent previously known.

physical and chemical condition required for its effective action as a drying agent. When water is present in any proportion in an organic liquid, and the mixture is brought into contact with the new desiccant, the above reaction takes place instantaneously and the amount of water required for the reaction, if present, is permanently removed from the liquid.

If the amount of water present in the liquid is appreciably less than 6.6 per cent of the weight of the desiccant used, the liquid is rendered anhydrous.

STABILITY OF HALF-HYDRATE

In the earlier paper (*3*) and also in the work of Shenstone and Cundall (*5*) it was shown that, while calcium sulfate half-hydrate heated in dry air begins to lose water slowly at 60° to 70° C., when heated in ordinary air containing water vapor this dissociation does not take place below 100° to 107° C. Furthermore, Davis (*2*) has shown that the vapors or liquids other than water (toluene, xylene) have the same effect as water vapor in raising the dehydration temperature of the half-hydrate to 100° C. or above. In the present work in all cases in which the dried liquid was separated from the desiccant by distillation, the whole bulb of the distilling flask was submerged in a water bath which was commonly maintained above 90° C. and frequently reached the boiling temperature. In no case was evidence obtained of contamination of the distillate by water expelled from the exhausted desiccant.

The method selected in any case depends, therefore, chiefly on the boiling point of the liquid to be dried. Thus, liquids boiling below 100° C. may be completely dried by being brought into contact with the granular desiccant in a