



ON THE NATURE OF COLOR IN WATER

A THESIS

by

Thorndike Saville

1917

TABLE OF CONTENTS

<u>Subject</u>	Page
Introduction	1
The Present Conception of Color in Water	2
The Nature of Colloids	3
Typical Colloids	4
Application of the Colloidal Theory to Water	8
Description of Apparatus	12
Description of Experiments	13
Experiments on Tea Extracts	13 a
Experiments on Colored Waters	17
Theory of the Colloidal Action of Alum in Decolorization	20 (footnote).
Experiments on Decolorization by Dialysis	28
Change in Color with Storage	29
Colloidal Theory of Color in Water	30
Decolorization by Sand Filters	32
Decolorization by Flocculation with Electrolytes	33
Decolorization by Storage	34
Influence of Alkalinity and Iron on Color	38
Acknowledgments	40
Bibliography	41

Illustrations

<u>Number</u>	<u>Subject</u>	<u>Page</u>
Plate II	U-Tube showing Cataphoresis of Tea	14a
Figure 1.	Diagram, showing movement of charged particles in U-tube when subjected to cataphoresis	20a
Plate III	U-Tube showing results of cataphoresis of Marlboro water after 250 hours	25a

Tables

1	Experiments on Tea Extracts	13a
2	Experiments on Water	17a
3	Change in Color with Storage	29a

Summary.

The studies reported in this thesis were undertaken to discover the chemical and physical properties of the coloring matter in natural waters. The results of the investigations have seemed to prove that coloring matter in water is in the colloidal state, and that it exhibits definite and characteristic properties which substantiate this contention.

A brief synopsis of the more important facts regarding the nature of colloids is presented. An outline is then given of the criteria which must obtain in order to apply the colloidal theory to color in water.

The results of the experiments performed in the laboratory by subjecting various waters to cataphoresis are described and tabulated. The results are interpreted on the basis of the colloidal theory.

Finally, there is presented a definite statement of the colloidal theory of color in water, based upon the results of the studies undertaken. This theory is then applied to interpret decolorization of drinking water by the several processes ordinarily employed.

A bibliography is appended, giving references to earlier studies upon the nature of color in water and to treatises upon the theory of colloids.

ON THE NATURE OF COLOR IN WATER.

By Thorndike Saville.

The writer has been engaged in a study of the problem of color removal from water, and in connection with the experiments which he has carried on, application has been made of some of the newer ideas of physical chemistry. The investigations described herein were undertaken with a view to proving or disproving the colloidal theory of color in water, and the discussion of results and conclusions are largely confined to that problem.

The question of color removal from public water supplies is being studied by many engineers. It is not so much a question of hygiene as of esthetics; not so much a provision to safeguard the health of a community as to cater to that psychological attribute which makes a clear and colorless water seem more salubrious than a turbid or colored water.

Present knowledge concerning the nature of color in water is far from satisfactory. From this lack of information there results the use of inadequate and often troublesome methods of removing color from

public water supplies. The studies reported in this paper are, therefore, only a contribution to the larger study of color removal, and they are presented as offering possible new departures in the technique of color removal practice.

The investigations made by the writer have been only upon waters from localities along the Atlantic Coast.

The Present Conception of Color.

The origin of the brown color of water is generally considered to be due to chlorophyll or its allied products derived from dead and decaying vegetation. Carbon, hydrogen, oxygen, and iron have been shown to be important elements of the coloring material. In general, the greater the amount of iron in a water, the greater will be its color. The color is usually some shade of brown, either yellowish or greenish brown; the change from one to the other often being seasonal.

Until comparatively recently, the physical nature of the color in water has received little attention. It used to be stated that (1)* "color is due to substances in solution, while turbidity is due to substances in sus-

* Figures in parenthesis refer to titles in the bibliography appended at the end of the paper.

pension." Moreover, (2) "tannins, glucosides, and their derivatives are doubtless present Carbon is the important element in its composition, and the color varies in amount very closely with the 'oxygen consumed.'" That "coloring matter (in water) is similar to, and possibly identical with, the coloring matter in tea" (1,2) has been generally accepted as a satisfactory explanation of the character of the coloring matter. These statements represented the current views on the question of the nature of color in water which have been held until lately. Recently studies have been made which will doubtless cause these earlier theories to be somewhat modified.

The belief has been slowly gaining credence that coloring matter in water is essentially colloidal in nature, and does not primarily exist in true solution. It is the aim of this article to show that color in water is certainly in the colloidal state, and that it exhibits definite and characteristic electrical properties which substantiate this contention.

The Nature of Colloids.

To make more intelligible the discussion of the material presented in this paper, a brief résumé

of the underlying theory is attempted in the following paragraphs. This is the more desirable since, to the writer's knowledge, no such statement of the colloidal theory as applied to color in water is available, except in two somewhat contradictory articles by Catlett (3,4).

At the outset it is important to define a colloid. The whole study of colloids is of such recent development that the nomenclature is as yet unsettled and often contradictory. The terms given below have been taken from the latest writers on the subject, and indicate the most recent views.

"A colloidal solution may be defined as a suspension, in a liquid medium, of fine particles which may be graded down from those of microscopic to those of molecular dimensions. The one property common to all such solutions is that the suspended matter will remain almost indefinitely in suspension in the liquid, the natural tendency to settle due to the attraction of gravitation being overbalanced by some other force tending to keep the small masses in suspension(5)." It has been shown that nearly all substances exist in the colloid condition if finely enough divided or properly prepared, and hence we now speak of substances as being in the colloidal state rather than of certain substances as colloids. The size

of particles to be in the colloidal state is generally taken to be from 0.001 mm. to 0.0000001 mm.

There are two major classes of colloids: (a) viscous, gelatinizing mixtures, not readily coagulated by salts, such as gum arabic, gelatine, glue, etc.; and (b) non-viscous, non-gelatinizing, readily coagulable mixtures. The first types are known as emulsoids, and may be considered as suspensions of one liquid in another liquid, as globules of fat in water. Those of the second type are called suspensoids. The latter consist of very finely divided particles in suspension in a liquid, and as color in water is supposed to exist chiefly in such a state, this is the only class of colloids which we shall consider. It is probable that the color in some waters, and possibly some of the color in all waters, is in the emulsoid state. The conclusions arrived at in this paper, however, are thought to be valid whether color in water is conceived of as a suspensoid or an emulsoid colloid.

Color in water is postulated as ordinarily a suspensoid colloid. The colloid particles, though invisible to the eye or under the microscope (colored water is often quite clear), are visible in the Tyndall ray (6). This is a device which makes use of a beam of

reflected light passed through the colloid solution. The colloid particles are thereby rendered visible. The phenomenon is similar to that by which dust particles in the air, ordinarily invisible, are made visible in a beam of sunlight. If the illuminated particles be now viewed through a microscope, their character can be ascertained. This combination is known as the ultra-microscope.

It was early found that ordinary suspensoids moved to one or the other electrode when an electrical current was passed through the liquid. This phenomenon has been called cataphoresis. The electrode toward which the suspensoids move is dependent upon the character of the charge which they carry, those negatively charged moving to the anode (and being called anionic suspensoids), while those positively charged move to the cathode (and are called cationic suspensoids). Certain substances when suspended in a colloidal state in water exhibit these characteristics, and in the following discussion it will be well to have in mind certain typical suspensoid members of each class* (5).

* Anionic Suspensoids

1. Sulphides of arsenic, antimony, and cadmium.

Cationic Suspensoids

1. Hydrates of iron, chromium, aluminum, copper, zirconium, cerium.
(Con. on next page).

"The fundamental assumption is that when a particle suspended in a liquid becomes charged, there exists about it a double electric layer; when the particle is negatively charged, there is a layer of negative electricity on the surface of the solid particle, while in the liquid immediately surrounding it there is a corresponding layer of positive electricity"; and vice versa for positively charged particles (5).

"In regard to the cause and character of the electrification, the phenomenon has been expressed by the term 'contact electrification'; the particles becoming charged by the rubbing of the moving particles of the liquid itself against the suspended particles" (5).

It has long been known that when certain salts such as $Al_2(SO_4)_3$ (the "alum" of water supply termin-

Note from Page 6.

Anionic Suspensoids

2. Suspensions of platinum, gold, silver, and mercury.
3. Vanadium pentoxide.
4. Stannic acid and silicic acid.
5. Aniline blue, indigo, molybdena blue, eosin, fuchsin, Prussian blue.
6. Iodine, sulphur, selenium, shellac, resin, kaolin, quartz
7. Starch, mastic, caramel, chloroform.
8. Silver halides.
9. Various oil emulsions.

Cationic Suspensoids

2. Bredig solutions of bismuth, lead, iron, copper.
3. Hofmann's violet, Magdala red, methyl violet, Bismarck brown, methylene blue.
4. Albumen, Hemoglobin, agar.
5. Titanic acid.

ology) are added to water, a flocculation and precipitation takes place.

Hardy (7) has shown that this is a colloidal phenomenon, the $\text{Al}_2(\text{SO}_4)_3$ forming aluminum hydroxide* which is in colloidal state. He formulates two rules for flocculation by electrolytes, as follows:

1. The coagulative power of a salt is determined by the valency of one of its ions. This preponent ion is either the negative or positive ion, according to whether the colloidal particles move up or down the potential gradient.

2. The coagulating ion is always of the opposite electrical sign to the particle.**

Application of the Colloidal Theory to Color in Water.

If the foregoing hypotheses are correct, and if we can apply them to interpret the nature of color in water, the following facts should be borne out in practice:

(1) If color is due to particles in the colloidal state, and such particles are merely minute masses of

*. It is now generally considered among chemists that the compound heretofore called aluminum hydroxide is really hydrous aluminum oxide having the formula $\text{Fe}_2\text{O}_3 + ? \text{H}_2\text{O}$, instead of $\text{Fe}_2(\text{OH})_3$.

** See footnote, page 20.

matter in suspension, then, given time, we ought to get decolorization by gravity alone. Under ideal conditions of quiescence and constant temperature, such might be the case. Practically the particles are so small, and are influenced to such an extent by convectional currents and wind, that it is quite feasible to keep them in suspension indefinitely by mechanical means alone. Add to this, that if, as we postulate, each particle carries a similar charge of electricity, there is a mutual tendency to repulsion, and in this way also the suspensoid phase is continued despite gravitative influence.

Moreover, as the velocity of a particle falling in a liquid is, according to Stokes (8), given by the formula $V = \frac{r^2(s-s')g}{gn}$ where r equals radius of particle s equals specific gravity of particle, s' equals specific gravity of liquid, n equals viscosity coefficient, and g equals gravity constant, it will be seen that the velocity of settling is proportional to the square of the radius. Thus in a particle having a size of 10 microns,* the size of a gold sol,** the velocity of settling under the influence of gravity alone and under ideal conditions

* 1 micron = 0.001 millimeter.

** See footnote, page 17.

is at the rate of 10 mm. per month. If, now, "the flocculation of particles increases the effective radius, flocculation must have the effect of greatly increasing the rate of sedimentation and, therefore, of clearing of suspensions (9). This is in fact the chief way in which flocculation is made manifest, and from this fact comes the common use of the word flocculation as signifying the rate of clearing of a suspension."

(2) If the color be due to colloidal particles in suspension, then they should be coagulated by electrolytes and in accordance with the laws of Hardy (page 8:). If all the color colloids carry the same charge, they mutually repel each other, and so tend to remain in suspension. If an electrolyte be now added carrying an opposite electrical charge, flocculation should occur. This is precisely what happens in greater or less degree, but in less simple relations.

As the writer hopes to show hereafter, color in water may carry either a positive or a negative charge. When the color is positively charged, it is removed by alum chiefly by mechanical action, and an overdose of alum will be needed to form a heavy enough precipitate to carry down the suspended color particles. In the case of negative color, both the positive aluminum ion from $\text{Al}_2(\text{SO}_4)_3$ and the positive aluminum hydroxide formed produce neutralization of the negative charge on the

color colloid. Hence there is in the case of negative color a flocculation from these causes as well as the mechanical action of the hydroxide. The underlying theory of these reactions is explained in detail in the footnote on page 20. It is a theoretical consideration and has not as yet been entirely substantiated by experiment.

If color is colloidal in nature, it should be concentrated upon boiling and evaporation of some of the water. This the writer has found to be true, an increase in color proportional to the concentration by evaporation being obtained, and also an increase in opaqueness of the liquid when viewed in the Tyndall ray.

(3) If the color be colloidal, then it should be electrically charged and move in an electric field. If a current be passed through the liquid, there should be a concentration of color at the electrode of opposite sign to the charge borne by the color suspensoid. With continued application of current, the color in the vicinity of the electrode of the same sign as the charge on the color particles should be reduced to zero. Finally, the discharge of color particles should occur at the electrode of opposite sign, with consequent flocculation and reduction of color there also. The experiments of the

writer have been conducted to investigate this phenomenon, and the results seem to entirely justify the conclusion that color in water must be chiefly colloidal in nature, and that it does obey the laws of cataphoresis as outlined immediately above.

Apparatus.

The apparatus used was simple, consisting at first of glass U-tubes varying in size from $\frac{1}{2}$ in. in diameter with 6-in. arms, to 1 in. diameter with 8-in. arms. These were filled with the liquid to be investigated. Electrodes of platinum wire were used, immersed directly in the liquid and connected to a 110-volt d.c. current. The amperage obtained was usually in the vicinity of one milliamperere.

Later a somewhat more elaborate tube has been used, fitted with a stopcock at the bottom, so that, when samples were being extracted, each side of the tube could be cut off and prevent any mixing of the liquid. It was found that in the simpler tubes there was a likelihood, especially when there was a precipitate, of causing a disturbance and mixing in the two arms when withdrawing a sample. The arrangement of wiring and general appearance of the apparatus is indicated by Plate II.

Description of Experiments

1. On Tea.

The investigation was begun during the winter, when highly colored waters were difficult to obtain in the vicinity. Earlier experimenters, Hollis, Brown, and Whipple, had all utilized leaf extracts in studies of color. In view of the fact that Hazen and others (2) so persistently advocated the similarity between the nature of color in tea and in water, the writer began his experiments with tea extracts.

At once the phenomenon of cataphoresis was evidenced. There was almost constantly throughout the experiment a decided difference in color between the two limbs of the U-tube, showing the particles to be moving toward one electrode and away from the other. To obey the laws of cataphoresis in their entirety, there should have been a continual decrease in color on one side, and a continual increase in the other side. That this is far from being the case is shown by Table 1. Here it is seen that for the first forty-two hours there was a sudden rise in color in both arms of the tube, the positive arm continuing to rise for sixty-eight hours and then dropping somewhat more slowly than the negative arm. Both arms, however, continue to lose color with

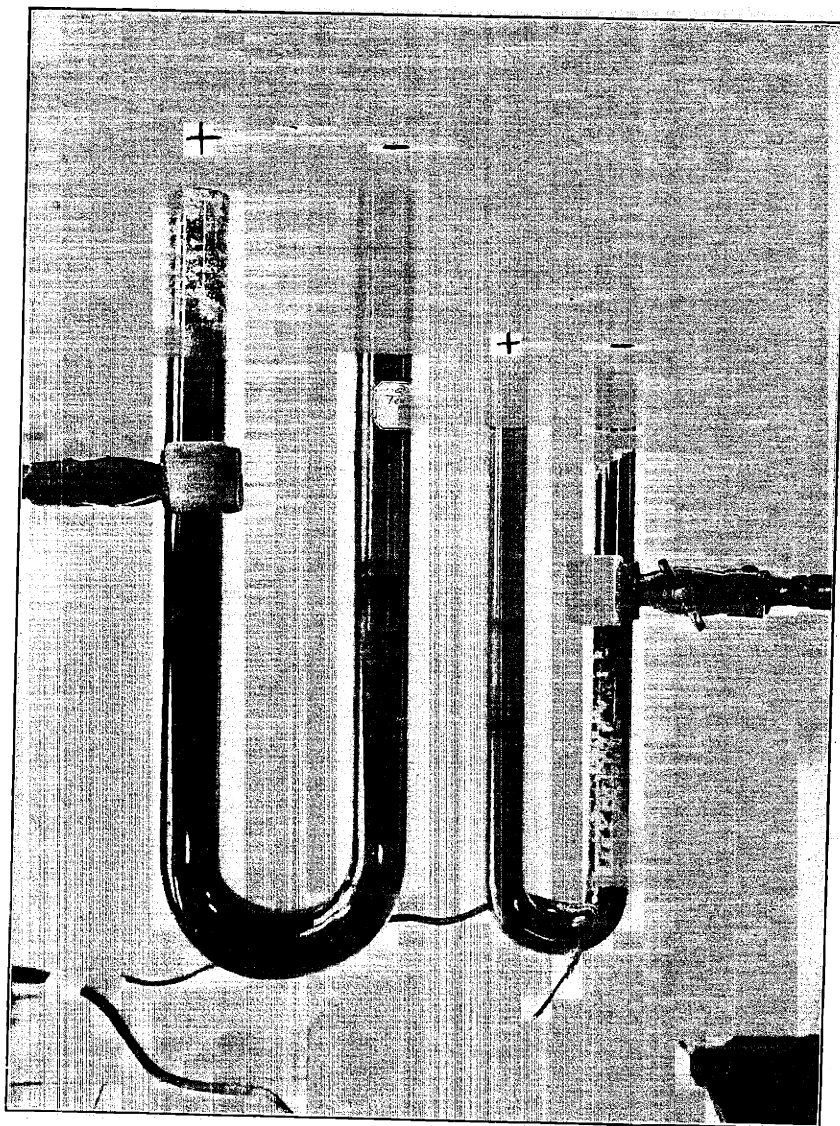
TABLE 1.
EXPERIMENTS ON TEA EXTRACTS.

EXPERIMENT No. 1.					EXPERIMENT No. 2.			BLANK.	
Large Tube. Platinum Strip.			Small Tube. Platinum Wire.		Large Tube. Platinum Wire.				
Hours.	Color, p.p.m.		Color, p.p.m.		Hours.	Color, p.p.m.		Hours.	Color, p.p.m.
	+Arm.	-Arm.	+Arm.	-Arm.		+Arm.	-Arm.		
0	2 750	2 750	2 750	2 750	0	4 300	4 300	0	2 750
3	2 900	3 400	6	5 200	5 100	42	3 200
22	4 200	5 000	11	5 500	5 000	261	6 000
42	5 700	3 300	5 200	5 200	20	6 700	6 000	384	7 100
68	5 800	2 300	5 500	1 000	28	7 000	5 500	504	7 100
76	6 000	2 300	5 500	1 000	34	8 600	3 800	648	9 600
93	6 200	2 400	5 100	800	48	8 000	3 500
125	5 500	2 800	3 300	3 300	56	11 000	3 500
149	5 500	3 700	2 700	300	63	9 600	3 200
214	3 700	3 300	1 200	200	72	10 000	2 700
261	3 600	3 100	300	50	80	10 000	2 400
288	3 400	3 400?	88	11 000	2 800
384	3 300	3 100	180	96	7 300	2 500
504	107	10 000	2 300
648	118	9 000	1 800
...	170	6 900	1 600

time, the positive arm remaining slightly more highly colored than the negative.

In Plate II, to the left, is shown a tube with tea extract after three hundred hours' run. The difference in color is noticeable, that in the positive arm being greater. There is also a heavy froth on top of the liquid in the positive arm, and in consequence there has been a holding back of the oxygen gas which is liberated at this electrode and a pressure developed which is manifest by the slightly greater height of the liquid in the negative arm.

The explanation of the sequence of events in this experiment is not entirely clear, but the writer interprets them as follows: The increase in color at first is due to oxidation of iron or some other element in the liquid, brought about by the oxygen at the positive pole. Some other electrochemical effects are doubtless active. The increase in color ceases when the chemical action producing it has been completed, and the cataphoresis, which has been masked, is now evident. The passage of particles toward the positive electrode is seen, and hence the colloid particles carry a negative charge. Discharge, flocculation, and precipitation at the positive pole occur, with reduction in color.



Tube at left shows tea extract after being subjected to cataphoresis for 300 hours. Tube at right shows tea extract after cataphoresis with copper electrodes.

Plate II

Color reduction is greatest in the negative arm, from which the particles move, and least in the positive arm, toward which they migrate.

The increase in the suspensoid phase in the positive arm increases the viscosity of the liquid, and consequently the oxygen gas escapes less readily and a froth forms. The formation of froth is characteristic of many cataphoresis experiments in water and indicates ordinarily the side to which the color moves. Large masses of flocculated material accumulated at the bottom of the positive arm, showing the color to be charged negatively.

In Plate II, on the right, is shown a tube with tea extract, which was subjected to cataphoresis with copper electrodes instead of platinum. Here there was a very rapid coagulation, the color decreasing from 4,600 to 250 in twenty-four hours. The copper goes into solution, forming an electrolyte, and the color is drawn to and deposited upon the anode.

A number of samples of tea extract were kept under differing conditions for observation as to changes of color. Very evidently there is a slow oxidation going on, as the color in the blank sample rises continuously. The results are tabulated below.

<u>Time</u>	<u>Unstoppered</u>	<u>Stoppered</u>	<u>Stoppered and Sterile</u>	<u>Unstoppered and Sterile</u>	<u>Sterile and in Dark.</u>
1 day	3000	3000	3500	3600	3300
3 days	3300	3200	3300	3400	3400
5 days	4500	4400	4400	5500	3700
8 days	7600	5200	5600		5200
2.5 mos.		10000	13000		13200
3 mos.		11000	29600		15200
8 mos.		6000	6900		8000

These show a progressive increase in color for three months, an increase greatest in the stoppered, unsterilized sample and least in the unstoppered, unsterilized bottle. That light plays little part is shown by the fact that the sample enclosed in a dark case has increased in color quite as much as the other samples.

A good deal of time was spent on these experiments, as it was supposed the behavior of water would be somewhat analogous. This was not found to be so, and the undesirability of drawing conclusions relating to color removal from anything but samples of natural colored water is evident. The preliminary experiments on tea did serve to indicate the general behavior of colloidal color in water and to familiarize the experimenter with the technique of his operations. Except for this, these experiments did not aid in the solution of the general problem.

change in the state of the iron content. The complex iron colloid is presumably oxidized to the hydroxide, which is insoluble.

The water from Mt. Auburn swamp was somewhat similar to the preceding, but its color was apparently almost entirely due to iron. Upon standing, precipitation took place after flocculation of the iron, and complete decolorization from an original color of 450 resulted in less than two months. This water, however, when fresh, was acid, and the color, therefore, carried a positive charge. For this very reason, the obedience to the laws of electrolysis as well as to those of cataphoresis was marked. The water has been especially mentioned on that account. This was the only water obtained which was acid, and was probably rather unusual for that reason.

In both the experiments noted above, there appears to be a double movement, in the nature of a circulation, in each arm of the tube. The nature of this movement in the case of the Mt. Auburn water is

Continued from page 17.

was applied to the liquid state while to the solid, jellylike form he applied the term "gel." If one of the two components was water, the two corresponding colloidal forms were a hydrosol and a hydrogel (10). These terms are now in common use.

shown in Fig. 1.* It will be noted that there are two positions of the top of the flocculated area, numbered 1 and 2. At first, the flocculent particles appear to go nearly to the electrodes, but very soon there appears a zone of decolorized water around each electrode, and further movement takes place in the space below this zone. It is presumed that the intensity of the electric field in this zone is strong enough to discharge the colloid particles when they approach its border, and so they flocculate and precipitate before reaching the electrodes. In this particular case all the colloid color particles should theoretically have moved from the positive to the negative electrode. Practically, the constriction in the tube was sufficient to hinder free passage, and certain particles being retained at the bottom took on, probably from contact, a negative charge and were drawn toward the positive electrode, where they were discharged. An alternating charging and discharging of particles in this way is the means which the writer has adopted to explain the frequent formation of floc in both arms of the tube, a phenomenon which occurs in many waters. With time, however, a

*This figure shows also the colloid movements when an acid is added to a colored water.

complete neutralization of all charge on the floc was obtained, and precipitation resulted with reduction in color. The froth appeared only upon the negative arm (in the case cited above where the color is positive), and there was finally a gradual movement from the positive arm to the negative arm of the floc which accumulated in the bottom. All the precipitated particles which cause color will, if the process be carried far enough, be found in the bottom of the negative arm if the color is positive, and vice versa. (Fig. 1.)

If, now, an acid, such as concentrated HCl, be added even in minute amounts to an alkaline water such as that from Bridgewater or Marlboro, the hydrogen ion of the acid, being positive, reverses the charge on the colloid.* The reaction is very rapid, and the

* Since water (H₂O) dissociates into H⁺ and OH⁻ ions, it is probable that among other charges carried by the color colloids in water is a positive charge due to the H⁺ ion of hydrogen. This ion may be in equilibrium with the H⁺ ion in the water in such fashion that

$$\frac{\text{H}^+ \text{ ion on colloid}}{\text{H}^+ \text{ ion in solution}} = \text{a constant}$$

and similarly for the OH⁻ ions if the adsorption law holds.

If, now, an acid, such as HCl, be added, which ionizes into H⁺ and Cl⁻ ions, the concentration of the H⁺ ions in the water is greatly increased, and to maintain the constant relation indicated above, the H⁺ ions on the colloids must also be

(Continued on page 21.)

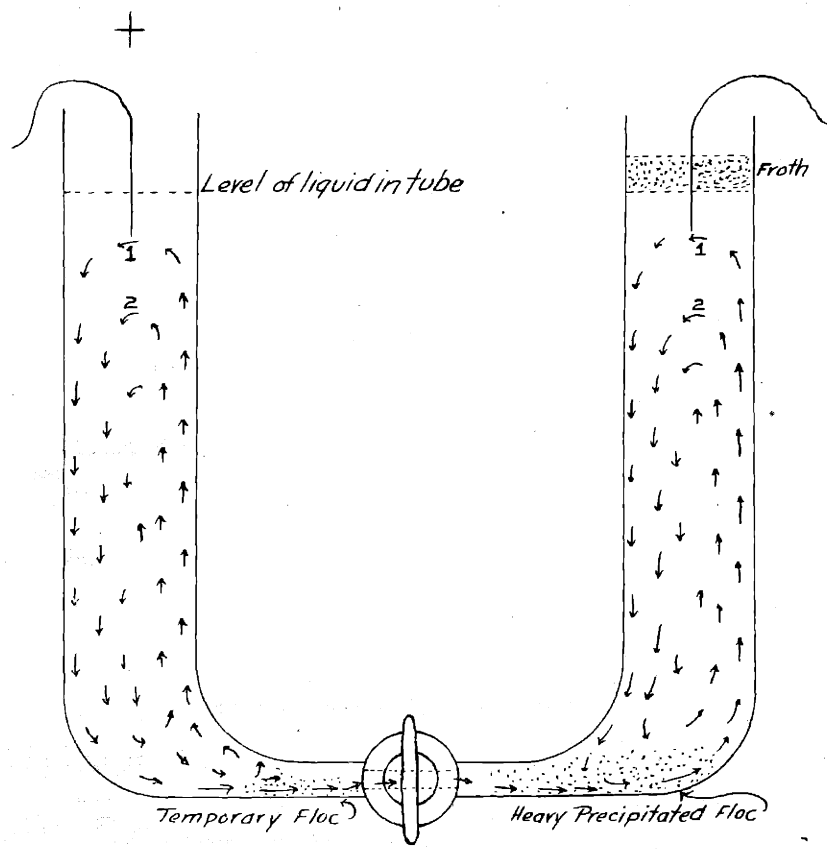


FIG. 1.

Diagram showing movement of positively charged colloid particles when subjected to cataphoresis.

electric field set up so strong that a floc appears at once in both arms and moves toward the negative electrode, on which is deposited a brown, jellylike substance. In twenty-four hours the color of the Bridgewater water after addition of 0.025 per cent. $\frac{N}{1}$ HCl was reduced from 840 to 0 in the positive arm and to 50 in the negative arm.

If, instead of an acid, the same amount of $\frac{N}{1}$ KOH be added to the water, exactly the opposite reaction

Continued from page 20.

increased. In this manner the colloid attains a stronger positive charge than it originally had. If there was only a negative charge, this will be discharged by addition of the H⁺ ions to the water, and the colloid will adsorb the positive ion. By so much as it increases its positive charge, its tendency to move toward the negative electrode is also increased. That the colloid takes up an H⁺ ion rather than a Cl⁻ ion is due to selective adsorption.

Similarly, when a base is added to the water, the colloid may absorb the OH⁻ ions (from, say, potassium hydroxide (KOH) which dissociates into K⁺ and OH⁻ ions), so that its negative charge is increased and it moves toward the positive electrode.

In the same way, when Al₂(SO₄)₃ (filter alum) is added to water, it dissociates into Al⁺⁺⁺ and 3 SO₄⁻ ions. The color colloid by selection apparently tends to adsorb the Al⁺ ions. If the color colloid be negatively charged, then the positively charged Al ion serves to cause discharge, and there results flocculation and reduction of color through precipitation of the colloids. Moreover, there is formed hydrous aluminum oxide (aluminum hydroxide), which is a positively charged colloid. This also serves to neutralize the negative charge on the color colloid.

When the color colloid is positively charged, it will not be discharged by addition of alum, and decolorization will not be obtained by the means suggested above. When, however, Al₂(SO₄)₃ is added to water, aluminum hydroxide

(Continued on page 22.)

takes place, with slightly less rapidity. There is here movement in the same direction as the normal water exhibits in this particular case. The rule is general, however, that, irrespective of the original charge on the color particles in the water, the color will move toward and flocculate in the negative arm of the tube when an acid is added; and a reversal of this phenomenon will take place if a base be added. This is in exact accordance with Hardy's law regarding (7) the direction of movement of a hydrosol in an acid or alkaline fluid; namely, that "an immeasurable amount of free alkali causes the proteid particles to move against the stream, while in the presence of an equally minute amount of free acid, the particles move with the stream. In the

Continued from page 21.

$\text{Al}(\text{OH})_3$ is formed, which produces a heavy flocculant precipitate. This, settling more or less rapidly as a matte, gathers up the colloid particles by adsorption and enmeshing, and hence under the influence of gravity the color is carried down with the precipitate, and reduction in color is obtained.

In waters negatively charged, both processes would seem to be effective in color removal; discharge of the negative colloid by the Al^+ ion and the hydroxide colloid, and the mechanical removal effected by the aluminum hydroxide. Under these conditions, color removal by alum is probably most rapid and effective. When the color colloid is positively charged, only the mechanical action of the hydroxide can be depended upon, and a larger amount of alum with possible overdosing is consequent.

one case, therefore, the particles are electro-negative and in the other are electro-positive."

What happens here is presumably that in the case where particles in the water are similarly charged to the acid or alkali which is added, these particles merely have their charge intensified and the reaction takes place in the normal direction with greater rapidity. In case the particles are of opposite charge to the acid or base that is added, the ionizing effect of the acid or base is sufficient to discharge the charge on the particles and then to charge them oppositely to the original charge. Or the difference in potential may become sufficient and the flow of current strong enough to attract the color particles to the electrode of the same electric sign as themselves. If the difference in potential be great enough, positively charged particles may be attracted to the positive electrode, and thus the phenomena described may also be explained, on this hypothesis.

In most of the waters investigated there was a reduction of color in both arms of the tube upon cataphoresis. The reduction in the arm carrying the electrode of opposite charge to that on the particles was always less than in the other arm, and the froth always appeared on the

arm toward which the colloid color particles moved. An explanation of the occurrence of froth has already been advanced. The cause for the reduction in color in both tubes is explained by two processes.

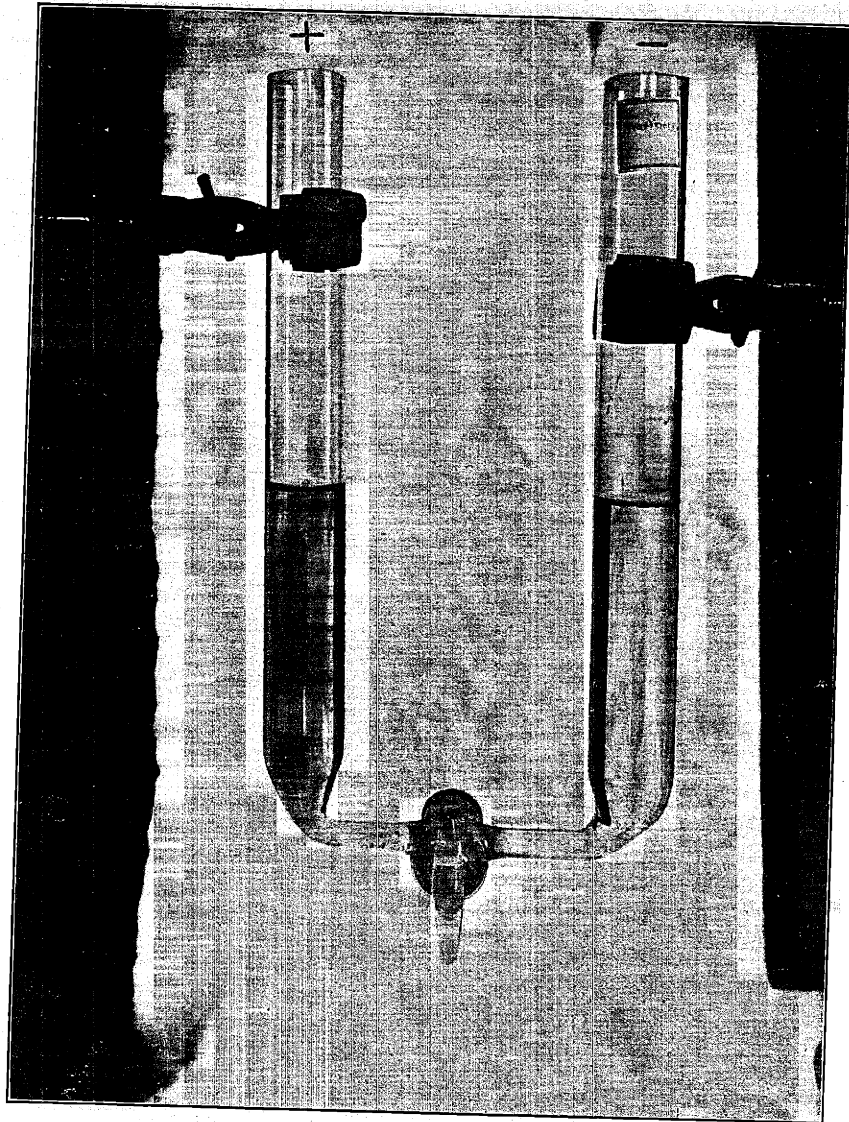
There is free oxygen given off at the positive electrode, and here the color particles (especially if they be negatively charged and so concentrated at that electrode) may be oxidized so as to lose their color. The most important cause, however, is supposed to be due to precipitation of the color colloids. There will be a reduction in color in the arm carrying the electrode of similar sign to the color colloids from migration of the colloids to the oppositely charged electrode. The slight reduction in color in the arm carrying the electrode of opposite sign to the colloids is due, as stated, to discharge in the vicinity of the electrode in this arm, and subsequent flocculation and precipitation. The flocculent particles are frequently not visible to the eye, but the reduction in color is usually evident, and after a time the accumulation of the precipitate in the bottom of the tube is conspicuous.

If all waters behaved in this fashion, with a reduction of color in both arms of the tube, the response of color in water to cataphoresis might not be considered

entirely conclusive. Fortunately, two waters were found in which the color obeyed almost exactly the theoretical laws of cataphoresis in colloid solutions. The Marlboro water is seen from Table 2 to have had an original color of 245. At the end of fifty hours the color in the positive arm had risen to 350, while that in the negative arm had decreased to 160, a mean of 255. After ninety hours, the colors in the positive and negative arms were 470 and 40 respectively, a mean of 255 again. After two hundred fifty hours, the colors were 450 and 0, a mean of 225, showing that the reaction was complete and precipitation had begun. The difference in color of the two arms of the tube is well illustrated by Plate III, taken at the end of two hundred fifty hours. The flocculated particles in the negative arm in the photograph are simply those few which the constriction in the tube prevents from passing to the positive arm.

It should be noted that not only is there a constant increase in color in the positive arm and corresponding decrease in the negative arm, but that the mean of the color in both arms is almost constantly very nearly that of the original water (245), as should theoretically be the case if there were no precipitation. If the current be kept on, precipitation will occur, a floe

W
181



Appearance of U-tube containing Marlboro water after being subjected to cataphoresis for 250 hours. Color in positive arm is 450, and 0 in the negative arm.

Plate III

forming in the positive arm. There is doubtless some earlier flocculation not apparent to the eye, and this accounts for the decrease observed in the color of the mean after two hundred fifty hours.

That this water follows so closely the laws of cataphoresis is doubtless due to the fact that both alkalinity and iron content are almost negligible, a condition not found in the other waters examined. There were, therefore, no electrochemical reactions upon the complex iron colloids which interfered with the cataphoresis of the color colloids.

The waters from Hopkinton Reservoir and the Ogeechee River exhibited similar properties, an increase of color in the positive arm and a decrease in the negative arm. As the first of these waters is from Massachusetts and the second from Georgia, the colloidal condition of color in water was not of local occurrence. The color in these waters, however, was somewhat less stable than that in the Marlboro water, and the reduction in color in both arms soon appears with flocculation and precipitation.

The water from Lost Pond in Brookline is interesting because of the apparent change in character of the charge carried by the colloid color particles. The color

is originally negatively charged, but after one hundred hours there has been a great reduction in color from neutralization and precipitation of the color colloids. It will be seen that at this point there is apparently a reversal of charge on the colloids remaining in suspension, and a consequent migration to and increase of the color in the negative arm. This reversal of color is explained in two ways. First, the normal negatively charged colloids have migrated to the positive electrode. Here most of them have been discharged and precipitated, but some have taken on a positive charge from this electrode and so move back toward the negative arm. In the second place, what little iron is present has become oxidized to the ferric state and become a positive colloid. Hence it tends to move toward the negative arm.

The water from Lost Pond showing these characteristics was obtained in the spring of 1916. Some water from the same place has been obtained this fall and does not show the variations noted above. This would indicate a more stable color and seem to show that the condition of the color in water varies at different seasons of the year.

In connection with the investigations outlined above, showing the colloidal nature of coloring

matter in water, mention should be made of certain experiments made by Mr. M. C. Whipple in the Laboratory of Hygiene and Sanitation at Harvard University in 1913. These experiments consisted of placing in flasks leaf extracts and natural waters having colors ranging from 100 to 150. Over the tops of the flasks, sheepskin parchment was tied and the edges paraffined to make watertight. The flasks were then inverted with the lower ends submerged in beakers of distilled water. In no case did the color of the distilled water increase appreciably, although there was change in alkalinity content, showing that dialysis took place. The color, therefore, apparently existed in the condition of particles too coarse to pass through the parchment, for if the color had been due to substances in solution, it would have passed through by dialysis. Moreover, illumination under the Tyndall ray showed the presence of a large amount of colloidal substances in the colored extract, but none in the distilled water even after three hours. The colloidal nature of coloring matter in leaf extracts, and in natural waters, is thus substantiated mechanically by these experiments, as well as indicated electrically by the investigations of the writer.

Change in Color with Storage.

Various waters were subjected to storage under varying conditions, the bottles being kept in the ordinary light of the laboratory.

The reduction of color by storage under room conditions was little unless the water contained a high iron content, which was easily brought into the ferric state and precipitated, as was the case with the Mt. Auburn water, and that from Bridgewater. In this event, the ferric hydroxide formed was a hydrosol and, upon contact or oxidation or by other means, was changed to the gel state and became a colloidal floc, when precipitation and reduction in color occurred.

In the open air, exposed to sunlight, there is always reduction of color in greater or less degree. The so-called bleaching action so frequently observed in the upper portions of reservoirs is possibly due in large measure to the action of the sunlight in breaking up the complex iron color colloid into some state in which its iron content may be oxidized and precipitated as described heretofore. The influence of sunlight upon waters of different degrees and state of color is well-illustrated in the last three waters of Table 3. The Mt. Auburn water having an iron content of 9 p.p.m., which

TABLE 3.

Locality.	Condition.	Original Color.	Storage, Days.	Final Color.	Per Cent. Reduction.
1. Lost Pond.....	Filtered, not sterile.	360	58	360	0
2. Lost Pond.....	Filtered, not sterile.	360	58	360	0
3. Lost Pond.....	Filtered, not sterile.	360	58	380	-5.5?
4. Lost Pond.....	Incubated in dark at 37 degrees.	360	58	340	5.5
5. Mt. Auburn Swamp.....	Natural condition.	450	60	0	100
6. Bridgewater Swamp.....	Normal condition.	1 020	58	690	32
7. Mt. Auburn.....	Exposed outside window sill.	450	35	0	100
8. Lost Pond.....	Exposed outside window sill.	360	35	120	66
9. Marlboro.....	Exposed outside window sill.	245	35	240	2?

was readily brought into the hydroxide state even under room conditions, was completely decolorized upon standing in the open air. The Lost Pond water, having an iron content of 2 p.p.m. and color colloids of iron which were less readily brought into flocculation, was decolorized 66 per cent. in the open air. The Marlboro water, with very low iron content, 0.75 p.p.m., and color due largely to other than the iron colloids, shows practically no reduction of color upon exposure to light. This would indicate that bleaching action per se by sunlight was in no large degree responsible for color reduction, but operated only so far as it produced chemical changes affecting the stability of the complex color colloids.

The growths of algae were pronounced in the Lost Pond water when exposed to sunlight, and did not occur under laboratory conditions. It is probable that these growths influence color removal, color colloids being retained on the gelatinous slime formed by them and so carried to the bottom.

Conclusions.

As a result of the experiments outlined above, the writer presents the following theory of the colloidal nature of coloring matter in water. The writer believes that the colloidal theory offers an explanation of many

of the obscure and contradictory behaviors of colored waters toward coagulating agents and toward the general processes of decolorization. The theory that coloring matter in water is in part at least colloidal in nature is not new, but the investigations and elaboration of this theory presented herewith are believed to represent more advanced data upon the subject than have heretofore appeared.

Color in water in large part exists in the form of colloidal suspensions of ultramicroscopic particles or "suspensoids." Some of the color may be due to colloidal emulsoids. A small part of the color is probably due to non-colloidal material, organic acids, and neutral salts in true solution. The colloidal coloring matter, whether suspensoids or emulsoids, carries an electrostatic charge. This charge may be positive or negative, depending on the character and source of the water, and varying in different waters. Color in water is usually due to negatively charged colloidal material.

These charged particles are of such minute dimensions that, if allowed to remain quiescent under the influence of gravity alone, they would remain suspended for very long times. Being similarly charged, they tend to mutually repel each other and remain in suspension indefinitely, a tendency which is strengthened by convectional temperature currents, wind, etc.

Since these particles carry an electric charge, and are in colloidal suspension, they obey the laws of cataphoresis when an electric current is sent through a colored water. The particles are attracted to the electrode of opposite sign from the charge which they carry. There they are discharged, flocculate, and precipitate, with consequent reduction in color of the water. This type of reaction may be, and often is, modified by electrochemical reactions, the reaction being theoretical only in those waters having little alkalinity or iron content.

When an acid is added to a colored water, the color migrates to the negative electrode. When a base is added, the color goes to the positive electrode. This is in accordance with the laws of Hardy outlined above.

Decolorization by Sand Filters.

Sand filtration has been found inadequate for the removal of color from highly colored waters. The degree of removal is very variable, depending on the water and the nature of the sand. A pure quartz sand (11) will remove little color, while sands containing much iron, aluminum, or manganese remove a large proportion of color. It is evident that the presence of iron and allied elements in a sand has an important effect upon

the capacity of that sand for color removal. In general, experiment has shown that about one third the color in water can be removed by filtration through sand. That more color cannot be removed may be explained on the hypothesis that the colloidal particles of which it is composed are so extremely fine as to pass in large measure through the smallest capillary pores in the sand. It is possible also that the color colloids removed by filtration are of opposite charge to the filtering medium. The color not removed may not have come in contact with the filter material or may carry the same electrical charge.

Decolorization by Flocculation with Electrolytes.

This is perhaps the most general method of clarifying colored or turbid waters. Either alum or ferric hydroxide and lime are commonly used as coagulants. The general principle of these reactions upon the basis of the colloidal theory has been explained at length.* To summarize: It may be said that where most successfully used, the action depends upon the discharge of a negative color colloid by the positively charged ion of the coagulating agent and the positively charged hydroxide

* Footnote, page 20,

which is formed. The consequent neutralization of the charged color colloids results in flocculation, precipitation, and decolorization. This process is materially aided by the mechanical removal of the color colloids by the hydroxide floc which is formed.

When clarification is obtained with difficulty, the reason is frequently that the color colloids in the water bear a positive charge. Hence they are not discharged by the positive ion of the dissociating coagulant. Under such conditions, the removal of color is supposed to be entirely a mechanical process resulting from enmeshment and straining out of the color colloids by the precipitated hydroxide floc.

It is well known that a high alkalinity frequently causes difficulty in color removal. This is explained by the fact that the elements causing alkalinity are negatively charged. If, then, the color also be negatively charged, a correspondingly greater amount of positively charged coagulant ion and hydroxide will be necessary to cause neutralization and precipitation.

By Storage.

Some engineers believe that the removal of color in water consequent upon storage for long periods of time in large reservoirs is due to the bleaching action

of sunlight. When decolorization occurs at considerable depths in the absence of light, oxidation has had to be adduced to explain the phenomenon.

That waters do become decolorized by storage is undisputed. It has been shown (1) that bleaching by sunlight is capable of removing color in water, but the writer doubts the competency of this process to explain the considerable color removal in reservoirs. If, as has been suggested in the foregoing statements, the color in water is largely due to particles in a colloidal state, the precipitation of such particles by storage is largely a matter of electrostatics.

The various streams tributary to a reservoir doubtless carry color particles having different charges. There is also more or less sediment in water, which generally is negatively charged. The mixture of all these variously charged particles in the reservoir probably tends to discharge certain of them, with consequent precipitation and decolorization.

Such, however, the writer believes to be only a minor cause of decolorization by storage. It was early shown by Hollis (13) and later by Whipple (1) that the increase in color with depth in reservoirs is due primarily to the condition of the iron content; that at depths the

iron is reduced and taken into solution; that upon rising to the surface in the spring, the iron is oxidized and adds to the color. That stagnation or storage will bring about an increase in color of the lower layers of the water which, given proper conditions of wind and temperature, may effect the upper layers, has also been shown by Whipple (1).

Notwithstanding this, there is in many reservoirs a decided decrease in color. What, then, is the cause of this decolorization, and how may it be explained by the colloidal theory? It seems probably that the iron content is the most important factor in this decolorization. Iron is important in sands for removing color; is a direct precipitant in the case of addition of electrolytes; is the factor upon which color removal by bleaching depends (see Table 3 and page 26); is the direct cause of color at the bottom of reservoirs; in short, iron is probably the chief element influencing the presence and removal of color in water. The iron probably does not exist in any such simple condition as the ferrous or ferric state. The iron content in color is supposed to exist in the form of certain organic compounds that are in colloidal state, - chemical compounds of extreme complexity. Due to many processes, of which oxidation

and electrostatic neutralization by other colloids are the most active, iron is brought into the ferric state, in which case it exists as a hydrosol and will be precipitated by clay or any other negative colloid. Otherwise, some slow chemical change is brought about so that the complex iron suspensoid is broken up into constituent particles which may carry opposite charges and so mutually precipitate each other, or which may be discharged by other differently charged colloids present in the water.

In general, it may be said that most coloring matter in water, whether due to iron or not, is charged; and that the color suspensoids mutually repel each other, tending to maintain their suspensoid phase. In large bodies of water, however, agitation by convectional and wind currents, oxidation, algae growths, etc., all tend to bring about contact between the color suspensoids and other colloidal substances in the water, many of which bear an opposite charge. There will tend to be discharge and neutralization. The particles will then flocculate and precipitate, and reduction of color will be apparent.

It has long been noted that, when certain turbid streams in the West carrying clay in suspension come into confluence with highly colored but clear rivers, there is sometimes a reduction in both color and turbidity in

the effluent stream. This is readily explained on the hypothesis advanced above if the color and turbidity bear opposite charges. In the same way, prospectors in the West state that muddy turbid pools of water can be cleared well enough to drink from merely by moving about in them a piece of cactus stalk. This phenomenon, too, is explained by the colloidal theory, since the cactus sap is acid and hence carries a strong positive charge. The negatively charged clay is thus neutralized and precipitated.

The writer believes, therefore, that not only is color largely due to charged colloidal particles, but that the state and degree of iron in the water is the controlling factor, both as to the permanence of the color and its ease of removal. The latter is undoubtedly much influenced by the alkalinity, - a high alkalinity making for difficulty in color removal. The alkalinity increases the negative charges and also possibly makes for electrostatic stability of the complex iron suspensoids. The addition of alkali to water in the same way seems to operate to prevent neutralization of the electric charge on the complex iron suspensoid, thus maintaining the suspensoid condition and preventing flocculation and precipitation.

If any one conclusion is evident from these investigations, it is that generalized statements and rules regarding color in water and color removal cannot be made. Every water is in this respect a law unto itself, and the problem of color removal from any given water can be intelligently approached only after detailed study as to the nature and electrical properties of the color in that particular water.

There is a great opportunity for further investigation along the lines of colloidal color in water, and that these investigations will undoubtedly prove helpful in the solution of the color removal problem is obvious. Such investigations, however, belong more properly to the water supply chemist than to the engineer. These problems must be approached with an unbiased attitude, for hitherto preconceived ideas have militated against a fuller understanding of the subject. While it is probable that all color changes and removal in water are not wholly due to the colloidal properties of the coloring material, yet it would seem that the colloidal theory may be looked to for a more complete understanding of the nature of color in water, and for a more satisfactory solution of methods for its removal than now obtain.

Acknowledgment.

The results of the investigation and studies presented in this monograph are the outcome of experiments carried on in the Laboratory of Sanitation and Hygiene at Harvard University. The subject was first suggested to the author by Prof. G. C. Whipple, to whom is due very sincere appreciation for many courtesies extended, for advice and criticism, and for facilities and equipment for experimental work. The writer is also greatly indebted to Mr. M. C. Whipple, instructor in sanitary chemistry at Harvard University, for his constant aid, advice, and helpful suggestions; to Prof. E. B. Millard, of the Massachusetts Institute of Technology, for advice regarding certain details of the chemistry of the problem; and to Mr. George Broussard, for help rendered in the laboratory.

B I B L I O G R A P H Y

-
- (1) The Microscopy of Drinking Water. George Chandler Whipple. New York, John Wiley & Sons, 1914.
 - (2) The Decolorization of Water. An informal discussion by G. C. Whipple, Allen Hazen, and others. Transactions American Society of Civil Engineers, Vol. XLVI, 1901
 - (3) Colloidal Theories, Applied to Colored Water, etc. G. F. Catlett. Engineering Record, Vol. 73, June 3, 1916.
 - (4) Colloidal Chemistry in the Removal of Color and Turbidity from Water. G.F.Catlett. American Public Health Association, 1916.
 - (5) The Physical Properties of Colloidal Solutions. E. F. Burton. Longmans, Green & Co., London, 1916.
 - (6) Floating Matter of the Air. John Tyndall, London, 1883.
 - (7) Conditions which Determine the Stability of Irreversible Hydrosols. W. B. Hardy. Proceedings Royal Society, London, Vol. 66, 1899.
 - (8) An Introduction to the Physics and Chemistry of Colloids. Emil Hatschek. P. Blakiston's Son & Co., Philadelphia, 1913.

- (9) The Phenomena of Flocculation and Deflocculation.
E. E. Free. Journal Franklin Institute,
Vol. 169, 1910.
- (10) The Chemistry of Colloids. W. W. Taylor. Longmans,
Green & Co., New York, 1915.
- (11) Woonsocket Water Works Reservoirs and Dam No. 3.
Allen Hazen. Journal New England Water
Works Association, Vol. 12, p. 32, 1897.
- (12) Decolorization of Water by Storage. Ralph H. Stearns.
Journal New England Water Works As-
sociation, Vol. 30, 1916.
- (13) Relation of Color to Character of the Water. F. S.
Hollis. Journal New England Water
Works Association, Vol. 13, 1898.
- (14) The Physical Properties of Water. Allen Hazen.
Journal New England Water Works Asso-
ciation, Vol. 17, 1903.
- (15) Removal of Coloring Matter in Water. R. S. Weston.
Journal New England Water Works Asso-
ciation, Vol. 16, p. 160, 1902.
- (16) Report to the Massachusetts State Board of Health
on the Metropolitan Water Supply.
Desmond Fitzgerald, 1895.
- (17) The Effect of Storage upon the Quality of Water.
F. P. Stearns. Journal New England
Water Works Association, Vol. 5, 1890.
- (18) Electro-Chemistry. Heinrich Danneel. John Wiley
& Sons, New York, 1907.

- (19) The Technical Control of the Colloidal Matter of Clays. H. F. Ashley. Technologic Paper 23, United States Bureau of Standards, 1912.
- (20) Salts, Soil Colloids, and Soils. L. T. Sharp. Scientific American, Supplement, No. 2101, April 8, 1916.
- (21) Problems in Smoke, Fume, and Dust Abatement. F. G. Cottrell. Smithsonian Reports, 1913.
- (22) The Purification of Ground Waters. R. S. Weston. Transactions American Society of Civil Engineers, Vol. LXIV, 1907.
-