PROJECT REPORT FORM

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NOTE BOOK 155
PAGE 46300 TO 46311
SIGNED *Herbert L. Davis*
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The Precipitation of Aluminum Oxide

In view of our major interest in aluminum oxide it seemed wise to begin experimental work on this project with a fundamental investigation of the effect of alkaline materials, and of pH changes on its precipitation. In order to have materials of known composition, the Analytical Department made an analysis of a 5 lb. bottle of Merck Aluminum Sulphate Lot No. 32097.

The alumina and sulphur trioxide were determined gravimetrically in the usual way and also by a thermal decomposition I suggested in 1932. This involved heating the original salt to $400^{\circ}C$. for 3 - 4 hours to drive off water, then a further heating to $1000^{\circ}C$. for 4 hours drove off the sulphur trioxide leaving alumina residue.

	Al_2O_3%	SO_3%	H_2O%
Theoretical	15.31	36.04	48.65
Gravimetric	16.75	37.87	45.38
Thermal Decomposition	16.97	37.69	45.34
Average of Inst. Detn.	16.86	37.78	45.36

The theoretical composition is for $Al_2(SO_4)_3 . 18H_2O$. It is clear that Merck product is a basic salt containing more alumina than is equivalent to the SO_3 and less water than the theoretical. Since in this work we are interested in the aluminum concentration, the formula was calculated as follows:-

$$Al_2(SO_4)_3 . 18H_2O - Al_2O_3 . 3SO_3 . 18H_2O - M.W. 666$$
$$\text{Merck product} - Al_2O_3 . 2.86SO_3 . 15.24H_2O - M.W. 605$$
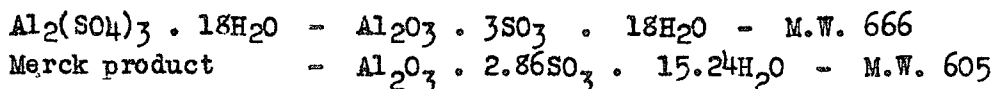
It is clear then that if one weighed out this "Merck Reagent" salt, he would have just about 10% more aluminum than he would calculate on the basis of 666 as the molecular weight. In all probability commercial alum differs even more than this from the theoretical. The Merck salt (60.5 g. gave a liter of 0.1 Molar or 0.6 Normal with respect to aluminum) dissolves to give a clear solution while the commercial salt betrays its even more basic character by a marked turbidity which soon settles as a precipitate in the solution. The Merck salt on extensive dilution in tap water develops a marked turbidity as a result of hydrolysis.

Although there seems some question as to whether the Glidden Nelio Resin is a typical paper makers rosin, it has been used so far in this work. It was tested by the Analytical Department, using a large sample taken directly from the barrel on the bridge.

Nelio Resin	
Acid Number	160.3
Saponification Number	180.0
Unsaponifiable Matter	8.72%

The acid number indicates the resin to be about 86.3% abietic acid. This plus the unsaponifiable portion equals 95%, leaving 5% for the esters requiring hot alkali for saponification. Subject to revision later, the following development has been made from the saponification number data.

1 g. Nelio Resin ≡ 180 Mg K OH ≡ 128.3 Mg NaOH ≡ 170 Mg Na_2CO_3

311.8 g. Nelio Resin ≡ 40 g. NaOH ≡ 53 g. Na_2CO_3 ≡ 62 g. Na_2CO_3 . H_2O

If this last weight of resin were saponified with the alkali shown and diluted to one liter, one might call this a liter of Molar (or Normal) neutral rosin soap. This would be about a 30% resin solution, and would not be stable (Lorenz says that 5% is about the maximum stable solution). One tenth of this weight of resin saponified with the 4 g. NaOH to give a dark brown liquid which was diluted to give a liter of 0.1N Nelio resin soap.

Alum Plus Sodium Hydroxide

In the experiments reported below 5 cc. 0.6N alum solution was pipetted into a large test tube. The required volume of the alkaline solution was pipetted into a graduate, enough water added to total 45 cc. and the whole dumped into the large test tube. After mixing the tubes were allowed to stand overnight for measurement of the sediment and pH of the supernatant liquid and for tests for aluminum ions in the supernatant liquid. For this test in most cases "aluminon" reagent (aurin tricarboxylic acid) was used, and also the dropping of some ammonium hydroxide in the tube and observation of turbidity produced if there was residual aluminum in solution. The aluminon test is slightly more sensitive to very small amounts of aluminum. The table below outlines the effects observed, the amounts of alkali added being expressed in terms of equivalents of alkali per aluminum atom. Theoretically each aluminum atom requires three equivalents of NaOH for its conversion and precipitation as Al_2O_3.

TABLE I.
Alum + Sodium Hydroxide

	pH	Sediment Depth, cm.
0.06 N Alum only (no alkali)	3.45	-
1 Equivalent NaOH	3.94	2.0
1.25 Equivalent NaOH	4.05	2.7
1.5 Equivalent NaOH	4.11	3.3
1.5 Equivalent NaOH	4.05	2.8
1.8 Equivalent NaOH	4.20	4.6
2.0 Equivalent NaOH	4.32	4.0
2.0 Equivalent NaOH	4.35	5.1
2.1 Equivalent NaOH	4.42	5.1
2.2 Equivalent NaOH	4.67	5.4
2.25 Equivalent NaOH	4.86	4.3
2.3 Equivalent NaOH	5.11	5.7
2.4 Equivalent NaOH	5.79	4.6
2.5 Equivalent NaOH	6.43	4.8
2.6 Equivalent NaOH	7.01	4.5
2.75 Equivalent NaOH	8.46	5.0
3.0 Equivalent NaOH	9.68	4.3

This table includes results of three different runs which check quite well except for the volumes of sediment. The critical lower value for complete precipitation is about 2.2 equivalents giving pH 4.67. For this run, aluminon test was not used and there is almost certainly some peptized Al_2O_3 in the supernatant liquids of the last one and possibly two systems. An unexpectedly large dispersing effect was exhibited by ammonia so that this test fails in the alkaline systems. Above pH 5.1 there is no demonstrable aluminum ions in solution until the alkaline peptization occurs.

TABLE II.

			Alum + Sodium Carbonate		Sediment Depth
				pH	cm.
1.5	Equivalent	Na_2CO_3		4.03	3.0
1.75	"	"		4.13	3.9
1.8	"	"		4.13	4.0
1.9	"	"		4.20	4.2
2.0	"	"		4.30	4.7
2.0	"	"		4.28	4.2
2.1	"	"		4.42	5.2
2.2	"	"		4.62	5.2
2.25	"	"		4.79	5.5
2.3	"	"		4.84	5.5
2.5	"	"		5.25	5.9
2.75	"	"		5.55	6.5
3.0	"	"		5.92	6.5
0.1N Na_2CO_3				10.8	approximately

The critical system here is 2.25 equivalent soda ash per aluminum atom giving pH 4.8, and there is no evidence of repeptization since the pH is so low.

TABLE III.

				Alum + Sodium Resinate		Sediment Depth
					pH	cm.
0.15	Equivalent	Na	Resinate		3.47	4.3
0.30	"	"	"		3.57	6.5
1.5	"	"	"		4.11	11.5
1.75	"	"	"		4.18	11.7
2.0	"	"	"		4.27	12.5
2.25	"	"	"		4.37	13.3
2.3	"	"	"		4.25	14.2
2.4	"	"	"		4.32	14.3
2.5	"	"	"		4.50	14.3
2.5	"	"	"		4.32	15.2
2.6	"	"	"		4.57	15.3
2.75	"	"	"		4.93	14.2
3.0	"	"	"		6.35	14.2
0.1N Sodium Resinate					10.71	-

In this system complete precipitation of aluminum is achieved by 2.6 equivalents of sodium resinate giving pH 4.57. The results in this system appear greatly influenced by the conditions of preparation. Thus it appears probable that a hot resinate solution would give different results from the one at room temperature.

Another system about which there has been much discussion is the aluminum acetate system. Table 4 shows the effect of adding sodium acetate to alum. The first run made had to be doubted when it was found that a 0.1N Sodium acetate solution (C.P. reagent) gave a pH of 7.01 when it should show about 8.7. To prepare a solution of sodium acetate, some acetic acid was titrated with standard sodium hydroxide until the pH was 8.58. In spite of the lower alkalinity of the first solution the pH values with alum were only about 0.1 pH lower as shown.

TABLE IV.
Alum + Sodium Acetate

				First Run		Second Run	
				pH	Sediment Volume cm.	pH	Sediment Volume cm.
1.5	Equivalent	Na	Acetate	4.05	0.3	4.11	0.2
1.75	"	"	"	4.10	0.5	4.18	0.5
2.0	"	"	"	4.15	0.7	4.21	0.8
2.25	"	"	"	4.20	1.1	4.27	1.0
2.5	"	"	"	4.23	1.4	4.35	1.5
2.75	"	"	"	4.28	2.1	4.38	2.2
3.0	"	"	"	4.35	2.8	4.45	2.5
3.5	"	"	"	-	-	4.53	3.2
4.0	"	"	"	-	-	4.62	3.7
0.1N Na Acetate				7.01	-	8.58	-

All of these gave positive tests for aluminum ions in the supernatant liquids. Since 4.0 equivalent gave the least ppt., it appears possible that more salt and a pH higher than 4.6 would complete the precipitation.

It would appear that the 3.0 equivalent system at pH 4.4 represents as near as one can get to aluminum acetate and it is largely precipitated in this system (sulphate). Incidentally the preparation of these systems offer a splendid opportunity for a visual following of hydrolysis. When first mixed all these systems are perfectly clear and then in 5 - 20 minutes a visible turbidity appears which increases rather rapidly to agglomeration and precipitation. I have demonstrated before the coagulating effect of sulphate ions on alumina peptized by acetic acid. One could undoubtedly have clearer and relatively more stable systems by using aluminum chloride instead of sulphate. Conversely some acetic acid would peptize the precipitate observed here.

Borax was chosen as another alkaline salt, and for its interest in connection with prosize. Assuming the correctness of $Na_2B_4O_7 \cdot 10 H_2O$, 19.07 grams was dissolved to make a liter of 0.1 Normal borax.

TABLE V.
Alum + Borax

	pH	Sediment Depth cm.	Supernatant Liquid	Aluminon Test	Ammonia Test
1.5 Equivalent Borax	4.35	5.5	Turbid	Slight red	No
1.75 " "	5.16	6.2	Clear	Yellow	Change
2.0 " "	6.40	6.6	Clear	Yellow	in
2.25 " "	7.28	6.5	Clear	Yellow	any
2.5 " "	7.68	5.6	Turbid	Reddish	Tube
2.75 " "	7.87	4.4	Turbid	Reddish	
3.0 " "	8.00	3.4	Turbid	Reddish	

This shows a most interesting case of irregular series. With borax the aluminum is all precipitated between pH 5.16 and pH 7.28, but shows increasing turbidity above this, decreased sediment depth and increasing color with aluminon. The ammonia test appears to be inoperative here because its dispersing effect is sufficient when coupled with that of the borate ion to peptize the aluminum oxide. Thus some of the turbid supernatant liquid (1.5 system) with a few drops of ammonia actually cleared on heating. Careful addition of dilute HCl did produce a characteristic alumina precipitate in this system. In absence of aluminum the aluminon reagent is yellow, with a quantity of aluminum there forms a flocculent red precipitate, and with only a trace of aluminum the solution takes on a red color.

Conclusions

1. The alum - NaOH run confirms very closely my findings by a titration with hydrogen electrode in 1932.

2. The pH values produced by various equivalents are shown.

TABLE VI.
pH Values Produced by Various Equivalents

Equivalent	1.5	2.0	2.5	3.0	pH of 0.1N Solution
NaOH	4.1	4.3	6.4	9.7	13
Na_2CO_3	4.0	4.3	5.2	5.9	10.8
Na Resinate	4.1	4.3	4.5	6.3	10.7
Na Acetate	4.0	4.1	4.2	4.3	8.6
Borax	4.3	6.9	7.7	8.0	9.1

3. The equivalents of alkaline material and pH for complete precipitation of aluminum are:-

	Equivalents	pH
NaOH	2.2	4.7
Na_2CO_3	2.25	4.8
Na Resinate	2.6	4.6
Borax, less than	1.75	5.2
Na Acetate, more than	4.0	4.6

4. These data seem to indicate that aluminum trioxide is precipitated from an aqueous system when the pH exceeds 4.8 - 5.0.

    a. There is so far little demonstration of the effect of divalent or complex negative ions. If it be considered worthwhile, an additional run on borax to cover the pH between 4.3 and 5.1 is indicated, and possibly one on sodium acetate to go beyond pH 4.6.

    b. In these systems the carbonate must be present as the bicarbonate and the resinate may form an acid soap. It might be useful to investigate the effect of added sodium sulfate on the alum -- NaOH systems.

5. This work has this bearing on the size project work. It will be necessary to study the precipitation of alumina for addtion to the beater. Probably a positively charged alumina will be more effective in precipitating the rosin emulsion, and we now have the necessary data for completing that precipitation. Some of these precipitates will be more effective than others by reason of diminished aging, greater ease of dispersion.

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PROJECT REPORT FORM

PROJECT NO. 578

CLIENT Institute

REPORT NO. 3

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NOTE BOOK 155

PAGE 46312 TO 46320

SIGNED *Herbert L. Davis*

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Various Experiments in the Sizing Project

Solvent Sizing Using Aluminum Resinate.

For some time I have been studying the possibility of sizing with a solution of aluminum resinate instead of the more usual rosin. A wholly qualitative experiment demonstrated that good sizing could be thus obtained. 100 cc. 0.6N alum was treated with 400 cc. 0.1N sodium resinate. While 600 cc. would represent the equivalent amount of soap, this excess of alum was used in the belief that such an acid product should be superior. It is slightly short of the amount needed to precipitate all the alumina and would show pH 4.1 - 4.2. This voluminous precipitate was filtered on a Buchner, washed, air-dried, and ground up. The yield was about 15 g. as compared to theoretical 12 g. (water).

A small amount of this material dissolved readily in benzene. Strips of Scott towels were passed through the solution, dried in air. On testing with a drop of water the untreated towel is waterleaf, while the treated towel is hard sized, and the drop rounds up upon it almost as upon paraffin. A drop placed at the border between sized and unsized portions is rapidly drawn off the sized area and spreads in untreated fibers. It is suggested that if there be sufficient interest in this process to warrant more extensive literature search, there should be some measurements of size values achieved with varying concentrations of aluminum resinate in various solvents. Minton chooses CCl_4 or ethylene dichloride as not dehydrating fibers as alcohol does. They would be free from the fire hazard of benzene. Aluminum resinate has been used in benzene or xylene as a quick-drying lacquer. A fundamental test to be applied on paper is its resistance to aging -- a characteristic in which the Minton rosin-solvent sizing is defective. Various ratios of alumina to rosin should be tested.

Making Rosin Sizing Visible.

It would aid the study of sizing if one could detect in some way just how the sizing material finally lands in the sheet. Some years ago it was shown that if fat be stained red with Sudan III (a typical oil-soluble dye), the soap formed by its saponification would also be red, the free fatty acid is red, etc. This demonstrates the affinity of the dye for the fatty acid anion, and it was thought a similar method might increase the visibility of rosin size.

In the first trial of this, some alcoholic solution of Sudan III was mixed with 0.1N sodium resinate to form a red sol. This was diluted to 1% rosin and used in the usual way with 2 and 4% rosin size and 4% alum. The sheets produced are colored pink, and are well sized; but examination of the sheets under the microscope reveals no particles interpretable as sizing. The fiber suspension before sheet making was pink, and in a few cases some suggestion of the tiny dots described by Lee (1936)

was found. It appeared that the sizing material was too finely divided to be visible.

It was believed that better results would follow if one used a sample of rosin, colored with dye and then emulsified with as little alkali as possible to give a high free-rosin (Bewoid type) size. A sample of Nelio resin was thus colored deep red, but saponification with small amounts of alkali with the malted milk stirrer proved ineffective until about 50% of the theoretical amount of caustic had been added. There resulted a deep pink or red emulsion of poor stability and about half of the rosin unchanged.

Some pulp was sized with this emulsion, giving pink sheets of good color and sizing. Examination shows some aggregates of red material where fibers cross, but still fails with 430X magnification (Lee used 720X) to reveal rosin particles beyond question. The fibers showed considerable red drops entangled in the fibillar material of the sheet and a few fine dots on the fibers. Discussion with Dr. Kress suggested use of darker dye (Methyl violet base) both as a means of achieving the end sought, and of discovering if any such use of oil-soluble dye for simultaneous coloring and sizing of a sheet might have superior fastness or other properties.

Calgon Prevents Precipitation of Aluminum.

In connection with some work on the wax emulsion being carried on at the same time, the suggestion of Smith of Calgon, Inc. (1934) to the effect that calgon represses the precipitation of aluminum hydroxide until pH of about 8 in strong calgon solutions was of interest. In order to learn more about this phenomenon, the following results were obtained.

Table I.

Alum + Calgon

	pH At Once	pH 24 Hrs.	Precipitate	Supernatant Liquid
5 cc. 0.6N (6%) Alum + 45 cc. H_2O	3.5	3.3	–	–
5 cc. 0.6N Alum + (0.5 cc. 5% calgon + 44.5 cc. water)	3.3	2.9	0.2 cm.	Clear
5 cc. 0.6N Alum + (1 cc. 5% calgon + 44.5 cc. water)	3.1	2.8	0.8 cm.	Clear
5 cc. 0.6N Alum + (2 cc. 5% calgon + 44.5 cc. water)	3.0	2.6	1.2 cm.	Turbid
5 cc. 0.6N Alum + (5 cc. 5% calgon + 44.5 cc. water)	2.9	2.6	1.3 cm.	Turbid
5 cc. 0.6N Alum + (7.5 cc. 5% calgon + 44.5 cc. water)	3.6	3.0	None	Turbid
5 cc. 0.6N Alum + (10 cc. 5% calgon + 44.5 cc. water)	4.3	3.8	None	Clear
5 cc. 0.6N Alum + (20 cc. 5% calgon + 44.5 cc. water)	5.6	5.5	None	Clear
5 cc. (or 10 cc.) 5% calgon + H_2O to 50 cc.	7.5	7.8	–	–
50 cc. 5% calgon	7.3	7.8	–	–

It is to be noted that calgon, although itself very faintly alkaline, makes alum solution drop in pH from 3.3 to 2.6 and then to rise to 5.5 as the amount of calgon increases.

Table II.

Alum + Sodium Hydroxide + Calgon

		pH	pH of similar systems without calgon
{5 cc. 0.6N (6% Alum {5 cc. 0.1N NaOH		5.6	-
{10 cc. 5% Calgon + †{30 cc. water			
" + 10 cc. 0.1N NaOH		6.5	-
" + 15 cc. 0.1N NaOH		7.4	4.1
" + 20 cc. 0.1N NaOH		8.3	4.3
" + 25 cc. 0.1N NaOH		9.3	6.4
" + 30 cc. 0.1N NaOH		10.0	9.7

(All systems were made up to 50 cc.; 30 cc. 0.1N alkali represents the theoretical equivalent.)

The effect of calgon is here truly remarkable. Without calgon everyone of these systems would have had a bulky alumina precipitate. With the calgon every system was and remained perfectly clear, even though the pH rose to 10.0. Since alkali alone would repeptize alumina, it is now possible to prepare clear solutions of aluminum in some form at any pH . Such systems, containing calgon, no longer give any test for aluminum by ammonia.

They also fail to have the usual flocculating action of alum on the wax emulsion. When 50 cc. samples of a 0.02% wax emulsion were mixed with 5 or 10 cc. of a mixture made by diluting 5 cc. alum + 10 cc. calgon to 50 cc., there is no visible or microscopically apparent effect on the emulsion. These emulsions are at pH 6.0 and 5.8 respectively, and this is the only method I know yielding stable wax emulsion systems at this pH. One cc. of a similar alum solution without calgon would coagulate the emulsion completely. With calgon no amount of alum seems to affect the emulsion. On April 1, I found such wax emulsion-alum-calgon systems capable of rendering cotton water-repellent in a one-bath process. Today Mr. Johnson and I prepared a similar system with wax emulsion at pH 6.3 and at 7.5% solids.

The action of calgon (sodium hexametaphosphate ($(NaPO_3)_6$) in increasing the acidity of alum systems and of decreasing the acidity of alum-caustic systems appears quite mysterious. If there appear suitable applications, further work might be justified. It appears probable that calgon is able to lock up alumina from alum in a soluble complex and leave the sulphuric acid free. When all the alumina is thus cared for, excess calgon behaves as a mild alkali to raise the pH. The systems containing alkali may fall under the same explanation, coupled with the large repression of the buffer effect observed when alumina is precipitated in the usual way. Another way to consider its action is to observe that it effects precipitation of alumina (or something else) at pH 2.9, and it repeptizes alumina in some form at pH 3.8. Both of these are very low pH values for such a phenomenon.

Precipitation of Sodium Resinate by Alum or Hydrochloric Acid.

In the beater, the rosin-pulp system is treated with alum. It appeared worthwhile to investigate this for the later work. In all cases the systems were brought to 50 cc. as total final volume.

Table III.
Sodium Resinate + Alum

		pH At once	pH 24 Hrs.	Pre-cipitate	Super-natant Liquid
5 cc. 0.1N Na Resinate	+ 45 cc. water	9.8	9.3	-	Turbid
"	+ {2 cc. 0.1N Alum {43 cc. water	9.0	8.7	None	"
"	+ 3 cc. 0.1N Alum	8.5	8.2	4.7 cm.	"
"	+ 4 cc. 0.1N Alum	{ 7.8	7.4	7.8 cm.	"
"	+ 20 cc. 0.02N Alum	{ 7.6	7.4	8.2 cm.	"
"	+ 21 cc. 0.02N Alum	7.3	7.3	8.5 cm.	"
"	+ 22 cc. 0.02N Alum	7.0	7.0	8.6 cm.	"
"	+ 23 cc. 0.02N Alum	6.5	6.6	9.5 cm.	Clear
"	+ 24 cc. 0.02N Alum	6.1	6.2	9.5 cm.	"
"	+ 25 cc. 0.02N Alum	{5.5	5.5	10.0 cm.	"
"	+ 5 cc. 0.1N Alum	{5.2	5.3	9.8 cm.	"
"	+ 6 cc. 0.1N Alum	4.5	4.3	9.8 cm.	"

The agreement between the two runs can be seen from the values of the duplicate systems.

Table IV.
Sodium Resinate + Hydrochloric Acid

		pH At once	pH 24 Hrs.	Pre-cipitate	Super-natant Liquid
5 cc. 0.1N Na Resinate	+ {2 cc. 0.1N HCl {43 cc. water	8.7	8.5	None	Milky
"	+ 3 cc. 0.1N HCl	8.2	8.1	1.5 cm.	"
"	+ 4 cc. 0.1N HCl	{6.9	7.0	2.7 cm.	Turbid
"	+ 20 cc. 0.02N HCl	{6.7	6.8	2.0 cm.	"
"	+ 21 cc. 0.02N HCl	6.2	6.4	2.2 cm.	"
"	+ 22 cc. 0.02N HCl	5.7	5.9	2.4 cm.	"
"	+ 23 cc. 0.02N HCl	5.1	5.2	3.2 cm.	Clear
"	+ 24 cc. 0.02N HCl	4.4	4.3	3.0 cm.	"
"	+ 25 cc. 0.02N HCl	{3.9	3.8	2.8 cm.	"
"	+ 5 cc. 0.1N HCl	{3.7	3.7	2.7 cm.	"
"	+ 6 cc. 0.1N HCl	2.7	2.7	2.7 cm.	"

The end points for complete precipitation of rosin (as judged by obtaining a clear supernatant liquid) are:-

| With alum | 23 cc. 0.02N | (92% of theoretical) pH 6.6 - 7.0 |
| With HCl | 23 cc. 0.02N | (92% of theoretical) pH 5.2 - 5.9 |

A recent correspondent asked if there was any change in pH on standing after size precipitation in the beater. The data of Table III indicate that in the usual range such change is negligible. All tubes were open to air so that absorption of CO_2 would explain changes observed in the alkaline systems.

Examination of a few of these systems in the paraboloid dark field is of interest. The original sodium resinate before or after dilution is nearly optically empty, but on standing development of increasing turbidity in the diluted solution is matched by appearance of tiny (0.5 micron) particles in the dark field. The addition of small amounts of alum accelerates this process and produces also clumps of material and a dense cloud of material which in particle size or high hydration is just below the limit of resolution with 930X magnification. Possibly this cloud represents colloidal alumina hydrate in process of flocculation by rosin anions. The HCl systems are similar except that they lack this cloud appearance and have fewer clumps of material sorbed on the slide.

It is of interest that the same rather sharp end point is obtained for alum as for HCl in terms of equivalents required to precipitate the rosin. This might argue for the formation of aluminum resinate and free rosin acid respectively as the actual reaction occurring. If it were colloidal flocculation one would expect the precipitating power of alum and HCl to be quite different. It may be that even in this presumably neutral sodium resinate there is actually only 92% of the resin in the true ionic form. The large difference in pH in the final two systems argues in favor of colloidal sorption of the acids involved -- the HCl being less sorbed than the H_2SO_4.

Precipitation of Alumina for Beater Addition.

In order to minimize electrolyte content of the sheet, a separate precipitation of alumina was proposed. In terms of the earlier work 50 cc. 0.6N alum should require 230 cc. 0.1N sodium carbonate for complete precipitation and this would have alumina on the desirable acid side. Two lots were prepared in this way, in the first 0.5 g. Hy-flo Supercel was added to the alum solution before the carbonate was added. In the second the Celite was added after precipitation of the alumina. In both cases the celite speeded filtration markedly but there was little difference in the rates as above prepared. The filter cake (alumina + celite) was dispersed in water with some difficulty, and the suspension was passed through the hand homogenizer once. Both systems settled out rather rapidly and would require some addition to realize their full effectiveness. A little aluminum chloride or alum would help but would introduce unwanted electrolytes. Experiments are in progress to discover the effect of adding this alumina suspension to a pulp - rosin - acid system. Possibly peptization with 10% of the original alum would disperse the alumina so that it would be sorbed on pulp and would sorb a high free-rosin size.

Summary.

1. It has been found possible to produce good sizing by immersion of a sheet in a benzene solution of <u>aluminum resinate</u>. Such solvent sizing may possess advantages discussed in previous reports.

2. Attempts to render rosin sizing visible have given only partial success. Further work on this is planned.

3. Remarkable effects of calgon on alum and on alum-alkali systems are presented. Small amounts of the slightly alkaline calgon increase the acidity of alum solutions, larger amounts decrease the acidity. Calgon-alkali-alum systems have much higher pH values than the same systems without calgon. This shows some value in wax emulsion work.

4. Precipitation of sodium resinate by alum and by hydrochloric acid has been found complete below:-

For alum - 92% of the theoretical at pH 6.5
For HCl - 92% of the theoretical at pH 5.2

This is to be compared with the previous finding that complete precipitation of alum with sodium resinate (the reverse problem) required 87% of the theoretical resinate giving pH 4.6.

	pH Complete pptn.	Equiv. Amounts
Adding alum to Na resinate	6.5	5.2
Adding Na resinate to alum	4.6	6.3

On the basis of these experiments it would appear that the pH range 4.6 - 6.5 would represent complete precipitation of both alumina and rosin. As I understand it, this includes all the useful pH range for efficient rosin-alum sizing. The alumina-rosin ratio must have an important effect for usually about three times the theoretical amount of alum is employed.

5. A preliminary study of the separate precipitation of alum for use in the beater to minimize electrolyte content has been made.

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PROJECT REPORT FORM

Experiments on Sizing, Including Effect of Sodium Sulphate on Neutral Rosin Size.

Hydrolysis of Sodium Resinate

It has been observed on numerous occasions that, although the 0.1N (3%) neutral sodium resinate is clear yellowish in appearance, dilution of this to 0.01N solution is followed by a slow development of turbidity. Since most of these experiments have been done in tubes left open to the air, there was an excellent chance that absorption of carbon dioxide was responsible for this turbidity, precipitating the rosin. Duplicate tubes of 0.01N solution have been standing for two weeks, one stoppered and one open. The tube left open has decreased in pH from 9.5 to 9.0 and has developed several times as much turbidity as the stoppered tube (pH 9.36). The marked turbidity of the closed tube and the fact that in the paraboloid dark field there is little difference in appearance between the two samples -- both showing a dense cloud of very fine material in Brownian movement (the original dilute system was nearly optically empty) -- justify the conclusion that the 0.01N sodium resinate does undergo extensive hydrolysis. Although this represents a possible beater concentration of size, the speed of this hydrolysis is so slow as to be of minor significance in commercial practice. Since a normal hydrolysis would be expected to increase the pH, the mechanism of the opposite effect here is obscure.

Alum plus Duponol System

The idea back of this work was that since the sulfonated alcohol detergents such as Duponol are able to form soluble calcium and magnesium compounds, they might also aid in producing clear systems of aluminum ions at pH 5 - 6, which might be used to precipitate the wax emulsion without the possibility of repeptization. The Duponol behaves somewhat like a soap in producing a fairly clear 5% solution in warm water, and then, with time, producing a slow precipitation of considerable of the material from solution. On adding 5% Duponol to 5 cc. 0.6N (6%) alum there is at first an increasing, then a decreasing precipitate, and finally clear system.

Table 1.
Alum + Calgon

5 cc. 0.6N Alum + 1 cc. 5% Duponol				pH	
"	"	2	"	3.28	Small precipitate
"	"	3	"	3.35	Increasing ppts.
"	"	4	"	3.42	" "
"	"	5	"	3.49	" "
"	"	6	"	3.52	" "
"	"	7	"	3.56	Maximum precipitation
"	"	8	"	3.59	Slowly decreasing ppts.
"	"	8.5	"	3.62	" " "
"	"	9	"	3.64	" " "
				3.66	" " "

Table 1.
(Cont'd)

	pH	
5 cc. 0.6N Alum + 10 cc. 5% Duponol	3.66	Clear System
" " 12.5 "	3.72	Clear System
5% Duponol only	9.59	

Although this behavior of Duponol with alum was analogous to that previously reported for Calgon, the Duponol systems do not permit any alkali addition, nor more than a very slight dilution without producing immediate and extensive precipitation. While the Calgon-alum systems did not precipitate the wax emulsion, Duponol-alum systems are almost as effective as alum alone. Since, however, no way was seen of achieving clear aluminum systems at pH 5 - 6, this work was set aside at this point.

Staining Bewoid Size with Sudan III.

It was previously suggested that a stained Bewoid type size might be visible when precipitated on the fiber. When Sudan III is shaken or heated with some commercial Bewoid size, the size assumes a pink color. But in the microscope none of the rosin particles appear stained, so that apparently only a little of the dye is dispersed by the protein-soap present. The expectation that the dye would not pass through this interface to the rosin seems justified, and further efforts may be made later to prepare such a size using rosin previously colored by dye before its emulsification.

Sodium Sulphate Salts Out Rosin Size

In the formulation of this project, one of the objectives was to minimize the concentration of sodium sulphate in the beater, since it was believed seriously to interfere with sizing. An indication of a possible reason for this has been found in the surprising fact that the sodium resinate may be very extensively precipitated by merely adding neutral sodium sulphate.

Before presenting the experimental data, a resume of relevant calculations would be of interest. The Paper Makers Chemical statement is that 50 - 70 grains of sodium sulphate per gallon ruins sizing. The handbook gives the following relation:

1 grain / gallon $\equiv$ 17.1 parts per million $\equiv$ 0.0171 grams / liter
Thus, 70 gr./gallon $\equiv$ 1.197 grams / liter
Sodium sulphate has a molecular weight of 142, so that 1.42 grams / liter would be 0.01 Molor.

In the typical beater would be placed:

2,000 lbs. stock + 40 lbs. rosin + 80 lbs. alum + 40,000 lbs. water. Since the sulphate present is the deciding factor, it would be equivalent to 80 g. alum in 40 liters, or 1/8 mol. alum in 40 liters, or $\frac{1}{320}$ mol. in one liter. Since

each mol. of alum contains 3 mols of sulphate radical, this gives 3   mols
sulphate in one liter. It therefore appears that, as the beater 320
is made up with fresh water, the sulphate ion concentration is of the order of
0.01 molar. But such a figure is already 18% more than the 70 grains per gallon
figure given above as destroying size. As the white water circulates in a closed
system, it should pick up increasing concentrations of electrolytes, and this is
commonly advanced as explanation of the difficulties encountered. In the recent
run on such a closed system at Cornell Wood Products, the log sheet shows nowhere
as much as 2 grams of soluble solids per liter, and yet a single beater charge
should make its water have 1.42 grams Na_2SO_4 per liter.

There appear certain possible explanations of this discrepancy. The rosin size
is rarely a neutral size so that the sulphate ions must remain in solution along
with calcium and magnesium from the water and with hydrogen liberated by hydrolysis.
This, however, would not greatly affect the weight of soluble solids. Probably a
much more important factor is the sorption of the sulphate ions on the fibers and
particularly on the alumina. Even in alkaline systems, alumina is known to sorb
quantities of sulphate ions and this effect would be much larger in the acid systems
used for sizing. By the same token, these sulphate ions would be carried along
with the sheet and would tend to preserve its excess acidity as sulphuric acid.

Two problems are thus presented. The first of these is the discovery of the
mechanism by which sodium sulphate interferes with sizing, and of a method to
minimize this. The answer to this latter question may well be found only in
the general basis of this whole project - how to minimize electrolyte concen-
tration in the beater.

In the previous report, Table III showed the precipitation of sodium resinate
by alum additions. The obvious extension was to study the same precipitation
in the presence of sodium sulphate, using 0.1M sodium sulphate system to
emphasize the effects. Table 2 shows the results of such a run compared with
the same systems without the added salt. Previously, the production of a clear
supernatant liquid above a precipitate of aluminum resinate was taken as evidence
of complete precipitation of the rosin, but it was found that on treatment of
5 cc of these clear supernatant liquids with a drop of 5% HCl there were produced
additional precipitates. This was taken as a very sensitive test for some form
of finely dispersed rosin. Another interesting feature of these systems is the
immediately large precipitation when 5 cc M Na_2SO_4 be added to 5 cc 0.1N Na
resinate. On dilution with 40 cc distilled water, this precipitate disperses
slowly, but overnight is still several times more turbid than a comparable
system made by adding 5 cc M Na_2SO_4 in 40 cc water to 5 cc 0.1N Na resinate.
For the runs shown, the second method of adding the salt diluted with the alum
solution was employed.

Table 2.

Precipitation of Na Resinate by Alum in Presence of Sodium Sulphate

		pH	Supernatant 18 hrs.	HCl Test	pH	Super-natant	HCl Test
					Without Na$_2$SO$_4$		
5 cc 0.1N Na Resinate	+ 45 cc water	9.6	Sl.Turbid	Vol. floc.			
"	+ (5 cc M Na$_2$SO$_4$ (40 cc water	9.6	"	" "			
"	+ 5 cc M Na$_2$SO$_4$ + 3 cc 0.1N alum	8.3	Clear	Sm. floc.	8.5	Turbid	-
"	+ 5 cc M Na$_2$SO$_4$ + 17 cc 0.02 N alum	7.9	"	Less floc.			
"	+ 5 cc M Na$_2$SO$_4$ + 19 cc 0.02 N alum	7.4	"	Turbid			
"	+ 5 cc M Na$_2$SO$_4$ + 20 cc 0.02 N alum	7.2	"	Faintly "	7.7	Turbid	Floc.
"	+ 5 cc M Na$_2$SO$_4$ + 22 cc 0.02 N alum	6.6	"	Very " "	7.0	Turbid	Floc.
"	+ 5 cc 0.1 N alum	5.5	"	Clear	5.4	Clear	Clear
"	+ 6 cc 0.1N alum	4.8	"	clear	4.5	"	"
M Na$_2$SO$_4$ alone		7.04					

Observations of Table 2 are as follows:

1. At pH values **above** 5.5 the sodium sulphate definitely lowers the pH of the corresponding systems although it is itself neutral.

2. Testing for complete precipitation of resin; clear supernatant liquids without Na$_2$SO$_4$ -- 23 cc 0.02N alum (92% theor.); clear supernatant liquids with Na$_2$SO$_4$ -- less than 15 cc. 0.02N alum. This is misleading, however, for when tested by the HCl addition, there is about an equal faint turbidity in both systems with 22 cc 0.02N alum (pH 6.6), and clear systems with more alum and at lower pH values.

3. The conclusion from this is drawn that sodium sulphate changes the rosin into a form which gives a clear aqueous liquid at pH values where without the salt there would be considerable turbidity. In other words, it seems to have a dispersing effect on the rosin.

4. A further indication from the HCl test is that the 22 cc 0.02N alum alone is the last tube to produce an immediate floc. while with Na$_2$SO$_4$ no tube beyond 17 cc 0.02N alum shows a floc. On this basis, the Na$_2$SO$_4$ seems to aid the alum in flocculating the rosin.

In view of the conflicting interpretations possible in this Table, the following run was made on systems without alum to get a measure of the effect of the sodium sulphate.

Table 3.

Sodium Sulphate Salts out Sodium Resinate

		At Once		24 Hours		
		pH	Appearance	pH	Ppt.	Appearance
5 cc 0.1N Na Resinate	+ 45 cc H$_2$O	9.53	Slightly	9.19	–	Turbid
"	+(5 cc M Na$_2$SO$_4$ (40 cc water	9.53	increasing	9.36	–	"
"	+ 10 cc M Na$_2$SO$_4$	9.49		9.37	–	Max. Turbidity
"	+ 15 cc M Na$_2$SO$_4$	9.46	Slight Turbidity	9.15		Slight Decreasing Turbidity
"	+ 16 cc M Na$_2$SO$_4$	9.48		9.15	0.2 cm.	"
"	+ 17 cc M Na$_2$SO$_4$	9.48		9.15	0.3 cm.	"
"	+ 18 cc M Na$_2$SO$_4$	9.46	4 X as Turbid	9.17	0.5 cm.	"
"	+ 19 cc M Na$_2$SO$_4$	9.44	Milky ppt.	9.17	0.5 cm.	"
"	+ 20 cc M Na$_2$SO$_4$	9.41	" "	9.15	0.5 cm.	"
"	+ 25 cc M Na$_2$SO$_4$	9.32	" "	9.12	0.6 cm.	"
"	+ 35 cc M Na$_2$SO$_4$	9.34	" "	9.12	0.7 cm.	"
"	+ 45 cc M Na$_2$SO$_4$	9.34	Most "	9.10	0.7 cm.	"

In the first half-hour, tubes up to and including 17 cc (0.34 M Na$_2$SO$_4$) had about the same slight turbidity; beyond that there was marked increase in turbidity up to an immediate partial precipitation in 0.9 M Na$_2$SO$_4$. The pH change is too slight to be significant. This appears to be a straight case of slow flocculation, for in three days all tubes except the blank had become milky and produced some precipitate. In tube 35 and 45, the supernatant liquid appears quite clear and the HCl test shows that about nine-tenths of the rosin has been precipitated by the salt.

The attempt was then made to correlate this precipitation with other properties of the solution in an attempt to control the change. Table 4 shows such observations, using a new solution of sodium sulphate.

Table 4.

Properties of Sodium Sulphate -- Sodium Resinate Systems

	0.5 Hr. Paraboloid	1 Hr. Surface Tension	24 Hrs. Appearance	pH	48 Hrs. Surface Tension
0.1 N Sodium Resinate	Practically empty	38	Clear	-	-
5 cc 0.1 N Na Resinate + 45 cc water	& few aggregates	44	Turbid	9.5	39
" +(1 cc M Na$_2$SO$_4$ (44 cc water	"	39	Clear !!	9.5	34.6
" + 3 cc M Na$_2$SO$_4$	"	37	Turbid	9.4	33.5
" + 5 cc M Na$_2$SO$_4$	"	37	Turbid	9.4	33.6
" +10 cc M Na$_2$SO$_4$	"	37	Turbid	9.4	33.4
" +20 cc M Na$_2$SO$_4$	Great Cloud of Particles	37	Very turbid Some ppt.	9.2	33.1
M Na$_2$SO$_4$	Empty	-	-	6.1	

The slight increase in turbidity which develops in 0.5 hour is not associated with visible particles in the dark field until the 20 cc system whose opaque turbidity is due to a dense swarm of particles which grow continuously, and overnight develop particles 1 - 5 microns in diameter and look like a rosin milk emulsion. The surface tension data are similar to those we have previously had in the lab course by adding salt to ordinary soaps. The sodium sulphate salts out the sodium resinate, $0.06M$ Na_2SO_4 being enough to saturate the surface with the soap and achieve the limiting effect.

The persistence of tube 1 cc (0.02 M) as clear, showing no such turbidity as was shown by tubes on either side of it suggested that this might be a fundamental clue. Table 5 shows a check series confirming this observation.

Table 5.
Properties of Sodium Sulphate -- Sodium Resinate Systems

		M Na_2SO_4	6 Hours Appearance	Surface Tension	24 Hours Appearance
5 cc 0.1 N Na Resinate	+ 45 cc H$_2$O	0	Turbid 1	39	Turbid 1
"	+ (5 cc 0.1 M Na$_2$SO$_4$ (40 cc water	0.01	" 0.5	36.5	" 0.5
"	+ 10 cc 0.1 M Na$_2$SO$_4$	0.02	Clear	34.2	Clear
"	+ 15 cc 0.1 M Na$_2$SO$_4$	0.03	Clear	34.3	Turbid 0.1
"	+ 20 cc 0.1 M Na$_2$SO$_4$	0.04	Clear	33.7	Turbid 0.2
"	+ 25 cc 0.1 M Na$_2$SO$_4$	0.05	Turbid 0.5	33.5	Turbid 0.4
"	+ 30 cc 0.1 M Na$_2$SO$_4$	0.06	Turbid 0.75	33.4	Turbid 0.9
"	+ 45 cc 0.1 M Na$_2$SO$_4$	0.07	Turbid 1	33.5	Turbid 1.2

The turbidity estimates are personal estimates, referred in each series to the blank as 1, although in 24 hours the blank is about 4 times as turbid as in 6 hours. There is a slow drop in the surface tension from the time of mixing and comparison of the three duplicates in the two series showing that the result achieved in 6 hours is that found in 48 hours.

It seems probable that the failure of sizing with sodium sulphate in the beater may be associated with the persistence of clarity in systems which are so close to 0.02 M Na_2SO_4 which even after three days is most striking. If the only effect of the salt is to agglomerate the size, we could expect a loss in sizing as a result, but in the critical range the effect seems to be one of a dispersion - of clarification. The phenomena exhibit a striking analogy to those observed by Rhodes & Wynn (1937) in the detergent power of common soaps shown in Table 6.

Table 6.

Effect of Na$_2$SO$_4$ on Detergent Power of Soaps

Concentration of Na$_2$SO$_4$	pH	% Increase in Brightness	% Improvement
0.0	9.66	22.45	100
0.0025 M	9.65	25.8	115
0.0050 M	9.65	25.8	115
0.05 M	9.68	19.1	85

Something of the nature of Alexander's zone of maximum colloidality may be involved here, but the true explanation is still obscure.

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1. Sodium resinate when diluted to 0.01 N solution undergoes extensive hydrolysis with a development of considerable turbidity and a dense cloud of material visible in the dark field.

2. Duponol behaves like Calgon in producing clear systems with alum. Unlike Calgon, the Duponol-alum systems still give a test for aluminum and precipitate wax emulsion but are precipitated by dilution or alkali addition.

3. The Bewoid size cannot be stained directly with Sudan III.

4. Neutral sodium sulphate salts out sodium resinate.

    a. This is accompanied by only a slight change in pH (Table 3).

    b. It enables alum to precipitate rosin more readily as judged by clarity of supernatant liquid, but has no marked effect if the liquid be tested with HCl.

    c. In presence of sodium sulphate some of the sodium resinate is modified into a soluble not easily precipitated form.

    d. In systems of sodium resinate-sodium sulphate there is a marked maximum in this effect at 0.02 M Na$_2$SO$_4$ with 0.01 N sodium resinate.

    e. This maximum falls at just double the concentration of the sodium sulphate introduced by an average size precipitation in the beater.

    f. There is probably some relation between these facts and the sizing difficulties encountered in closed white water systems.

PROJECT REPORT FORM

The Effect of Sodium Sulphate on Rosin Sizing

FILED JUN 10 1938

This report will include a summary of the first handsheets made (4/26) in this project. For these sheets, Weyerhaeuser bleached sulphite pulp was beaten to a freeness of 520 cc at 1.54% consistency. The procedure adopted was to weigh out enough (650 g.) of the pulp suspension to contain 10 g. O.D. pulp for each batch. To the batch was added rosin and then alum with stirring by the malted milk mixer at a moderate rate, allowing about 3 - 5 minutes stirring between rosin and alum and after the alum addition. Then the batch was diluted to 1000 cc (1% pulp), stirred, and 170 g. taken for each of the four sheets. No attempt was made to control the pH of the water in the sheet mold, the 170 g. pulp suspension were poured in, stirred, and the water drained at once. Sheets were pressed between blotters and felts one minute at 100 lbs. and then dried 10 minutes on Williams drier. For all systems, the neutral sodium resinate (0.1 Molar or 3.12% rosin) was used. For the first two series a neutral turbid commercial aluminum sulphate was used, for all others the better standardized Merck aluminum sulphate (0.6N or 6.05% alum) was used. The pH values shown are for the 1% pulp suspension as it was poured into the sheet mold.

TABLE I.
Rosin plus Alum Sizing

	pH	Basis Weight	Size Currier Sec.	Size TAPPI Sec.
I A, Blank, no size, no alum	7.7	40.9	0.6	2.6
I B, Pulp + 2% Na Resinate, no alum	7.7	40.0	1.2	4.4
I C, Pulp + 2% Na Resinate + 2% alum	6.3	41.1	36.9	40.4
I D, Pulp + 2% Na Resinate + 4% alum	4.4	41.5	35.0	38.5
I E, Pulp + 4% Na Resinate, no alum	8.4	43.0	4.2	8.6
I F, Pulp + 4% Na Resinate, + 2% alum	6.5	42.9	42.8	43.3
I G, Pulp + 4% Na Resinate, + 4% alum	4.5	43.3	43.5	44.1

From this, the following conclusions are drawn:

1. There is fair agreement between the Currier (electrical conductivity) and the TAPPI (dry indicator) size values, the TAPPI values being generally slightly higher.

2. Four per cent rosin gives about 15% higher sizing than two per cent.

3. Four per cent alum is little better than 2 per cent; in system D it seems to give an excessively low pH.

In the next two runs, a study was made of the effect of sodium sulphate on sizing. This matter was discussed in the previous report with some test tube experiments demonstrating that sodium sulphate salts out sodium resinate and affects its precipitation by alum. It was also pointed out that in the beater, using 4% alum on the stock, there would be an initial concentration of 0.01 Molar with respect to sulphate ion and that this concentration is greater than the 70 grains per gallon said by P.M.C. to ruin sizing. The direct study of handsheet sizing reveals no such action even by amounts of sodium sulphate considerably larger. A preliminary run is shown in Tables II and III.

TABLE II.
Effect of Sodium Sulphate on Sizing

	pH	Basis Weight	Size Currier	Size Tappi
II A, Pulp + 2% Na Resinate + 2% alum	6.2	38.2	29.1	33.3
II B, Pulp + 2% Na Resinate + 4% alum	4.4	39.1	35.1	34.2
II C, Pulp + 0.02M Na$_2$SO$_4$ + 2% Rosin + 2% alum	6.2	38.4	33.9	33.8
II D, Pulp + 0.02M Na$_2$SO$_4$ + 2% Rosin + 4% alum	4.6	39.5	35.7	36.3
II E, Pulp + 0.2M Na$_2$SO$_4$ + 2% Rosin + 2% alum	5.8	39.4	19.8	33.3
II F, Pulp + 0.2M Na$_2$SO$_4$ + 2% Rosin + 4% alum	4.8	39.7	17.7	31.9

A second more extensive run on this is shown in Table III.

TABLE III
Effect of Sodium Sulphate on Sizing

	pH	Basis Weight	Size Currier	Size Tappi
III. A, Pulp + 2% Na Resinate + 2% alum	6.0	44.5	47.7	49.4
III B, Pulp + 2% Na Resinate + 3% alum	4.9	44.3	47.8	45.0
III C, 0.01M Na$_2$SO$_4$ + 2% Rosin + 3% alum	5.0	44.6	47.8	46.2
III D, 0.02M Na$_2$SO$_4$ + 2% Rosin + 3% alum	5.1	44.8	51.8	49.4
III E, 0.03M Na$_2$SO$_4$ + 2% Rosin + 3% alum	5.0	45.7	47.7	45.9
III F Discarded as obvious error				
III G, 0.1M Na$_2$SO$_4$ + 2% Rosin + 3% alum	5.1	46.2	31.1	48.2
III H, 0.2M Na$_2$SO$_4$ + 2% Rosin + 3% alum	5.0	45.2	25.0	48.2

In the following systems, Pulp, Na$_2$SO$_4$ + Na Resinate stood 4 hours before alum addition.

	pH	Basis Weight	Size Currier	Size Tappi
III I, No Na$_2$SO$_4$, 2% Rosin + 3% alum	4.8	43.3	41.9	47.3
III J, 0.02M Na$_2$SO$_4$, 2% Rosin + 3% alum	5.0	44.2	40.7	52.3
III K, 0.2M Na$_2$SO$_4$, 2% Rosin + 3% alum	5.1	44.6	24.0	47.2

In the examination of these results, two approximations are noted. The pH values are reported to only one significant figure although two are recorded. In adding the sodium sulphate to the 650 g. of pulp suspension, 13 cc and 130 cc M Na_2SO_4 were added to the systems called respectively (D) 0.02M and (H) 0.2M although dilution would make the actual concentration less than this in the systems when the rosin was added.

These conclusions seem justified.

     1. With 0.03M Na_2SO_4 or less, there is no demonstrable effect on either size value although this is more than three times the reputed upper permissible limit.

     2. It may be only a coincidence that the maximum sizing comes at (D) 0.02M Na_2SO_4 which is the concentration of salt previously shown to give the least agglomeration of sodium resinate alone.

     3. With 0.10M Na_2SO_4 or more the Currier size drops sharply but the Tappi value is unchanged. This appears due to an excessive amount of electrolytes left in the sheet so that the penetrating water becomes a far better conductor.

     4. If sheet B be taken as standard, the following comparison is made of the changes in size values (for Currier size).

	Blank	0.02M Na_2SO_4	0.2M Na_2SO_4
Alum added at once	Standard	+ 8%	-48%
Alum added after 4 hours	-12%	-14%	-49%

     5. It appears that dilution may effect an agglomeration of the sodium resinate, that small amounts of salt accelerate this favorably at first (D) and then excessively with time. The high salt concentration agglomerates the rosin immediately and time has no further effect.

     In the ordinary procedure where alum is added very shortly after the rosin, such changes would be unimportant; but, in a closed water system, if alum were added near the machine, such conditions might prevail.

     The three sheets shown in Table IV were made to demonstrate certain ideas. In the A and B sheets two rosin emulsions were used in which the rosin was dyed with Sudan III, in an attempt to render sizing visible in the sheet, while the C sheet was made by a separate precipitation of aluminum resinate.

TABLE IV.
Special Sheets

		pH	Basis Weight	Size Currier	Tappi
A.	Pulp + 4% Rosin (Red) + 3% alum	4.9	45.8	52.7	53.9
B.	Pulp + 4% Rosin (Red) + 3% alum	5.4	46.3	37.6	50.4
C.	Pulp + [4% Na Resinate + 3% alum] Separately precipitated	5.7	46.6	35.1	47.3

Although sheets A and B are colored pink, and this suggests the use of such oil-soluble colors for dyeing paper, the visibility of the rosin in the sheets has not been demonstrated. The C sheet represents my first attempt to achieve sizing by this method. To 100 cc water was added 5 cc alum solution and then 12.8 cc sodium resinate solution. This suspension of aluminum resinate was then dumped into the 650 g. of pulp suspension, stirred, diluted, and sheets made as before. No direct comparison can be made with any other sheet, but it is demonstrated that satisfactory sizing can be achieved by a separate precipitation of aluminum resinate. Many more sheets will show this in subsequent reports.

The general results of these experiments, performed over a month ago, are as follows:

1.   Reference values have been obtained for sizing of handsheets.

2.   It is demonstrated that handsheets sized in the presence of reputedly destructive amounts of sodium sulphate still do show good sizing. Excessive amounts of the salt do greatly decrease the value of the Currier size, but still have practically no effect on the Tappi size values.

3.   Delay in adding alum to pulp-rosin-sodium sulphate mixtures may decrease sizing in presence of moderate amounts of salt.

4.   It is possible to obtain good sizing by adding freshly precipitated aluminum resinate to pulp.

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PROJECT REPORT FORM

Further Sizing Handsheets Especially with Bewoid Size

In the origin of this project, a prime purpose was to produce effective sizing under such conditions that the electrolyte content of the paper should be a minimum. This was to be achieved by some such procedure as the separate precipitation of alumina, filtration, and then the addition of this alumina to the pulp-rosin mixture. A further idea to try was the separate precipitation of aluminum resinate, filtration, and then addition of this to the pulp. In Series IV and VI various procedures were followed using the sodium resinate solution, while in V, VII, and VIII similar experiments were run on the Bewoid size so kindly furnished by Dave Peterson of Bergstrom's on May 3.

In the tables will be shown the substances added, calculated on the weight of the pulp, and added in the order shown. Thus, for IV A - 625 g. x 1.6% gave 10 g. O.D. pulp. To this were added 6.4 cc of 3.12% sodium resinate (2% on pulp) and 3.3 cc of 6.05% aluminum sulphate (Merck) (2% on pulp). The additions shown in parentheses were mixed separately as indicated, filtered (or not), and added to the pulp. In IV D and in several systems thereafter it was found that a portion of the total pulp could be used as a filter medium. This portion was usually about one tenth of the total, and the filtered wet lap plus the precipitate was stirred into the rest of the pulp. Pulp used was Weyerhaeuser bleached sulphite beaten to freeness 540 - 550 cc.

Table 1. Sizing by various methods

		pH	Basis Weight	Size Currier	Tappi
IV.	A, Pulp + 2% Na Resinate + 2% Alum	6.1	41.3	44.3 s.	50.8 s.
IV.	B, " + " + 3% "	4.8	41.1	45.0	51.3
IV.	C, " + [100 cc water + 2% Na Res.+ 3% Alum]	5.0	42.1	42.4	48.8

The water, sodium resinate, and alum were mixed separately, stirred, not filtered, whole suspension added to pulp.

		pH	Basis Weight	Size Currier	Tappi
IV.	D, Pulp + [100 cc water + 2% Na Res. + 3% Alum]	7.2	41.8	9.8	12.2

The aluminum resinate was formed as shown, stirred, much of it ran through filter paper. The turbid filtrate was stirred up with about 0.5 g. pulp (50 cc) to be used and poured on same filter, giving more clear filtrate. This wet pulp + alumina resinate was shredded into the rest of the pulp, stirred, diluted to one liter, stirred 15 minutes.

		pH	Basis Weight	Size Currier	Tappi
IV.	E, Pulp + 3% Alum + 2% Na Resinate	4.9	42.4	43.8	43.9
IV.	F, " + " + 1% NaOH + 2% Na Resinate	7.9	42.4	28.9	32.1
IV.	G, " + 2% Na Resin + 1% NaOH + 3% Alum	7.9	46.3	29.6	34.8

Table 2. Sizing of Various Methods

			pH	Basis Weight	Size Currier	Tappi
VI.	A, Pulp + 2% Na Resinate + 3% Alum		4.7	41.7	45.6	47.1
VI.	B, Pulp + 3% Alum + 2% Na Resinate		4.8	41.3	36.8	38.2
VI.	C, " + 2% Na Resinate + 3% Alum + 0.6% NaOH		6.6	42.1	41.5	42.5
VI.	D, " + [2% Na Resin + 0.6% NaOH] + 3% Alum		6.6	42.3	35.7	37.9

The alkali precipitates the resin soap considerably. Even dilution does not clear the turbidity.

VI.	E, Pulp + [3% Alum + 0.6% NaOH] + 2% Na Resin		5.1	42.1	36.8	38.8

Alum and alkali were mixed separately in water and added to pulp without filtration.

VI.	F, Pulp + [100 cc. Pulp susp. + 2% Na Resin + 3% Alum, Filter]	7.5	41.4	16.3	21.1

The aluminum resinate was precipitated on about a tenth of the total pulp, filtered, and the wet pulp pad stirred into rest of the pulp. The filtrate contained unprecipitated aluminum as more sodium resinate gave a precipitate.

VI.	G, Pulp + [Pulp + 3% Alum + 2% Na Resinate, Filtered]	7.4	40.7	4.8	8.6

procedure same as in F except alum added before resinate

VI.	H, Pulp + [Pulp + 2% Na Resin + 1.5% Alum, filtered]	7.4	42.1	20.1	32.1

Still filtrate shows excess aluminum

VI.	I, Pulp + [Pulp + 2% Na Res. + 2.25% Alum, filtered]	7.3	41.1	12.4	18.8
VI.	J, " + [" + " + 4.5% " "]	7.3	40.2	12.8	20.5
VI.	K, " + [" + " + 1% NaOH + 4.5% Alum, fil]	7.2	41.4	14.9	25.8
VI.	L, " + [" + " + 2% " + 6% Alum, filt.]	7.0	41.0	30.0	39.6
	Original pulp suspension in tap water	7.7			

From these data, the following conclusions may be drawn.

     1. The usual method employing 2% rosin and 2 or 3% alum gives good sizing, but adding alum before rosin (IV E, VI B) reduces its effectiveness.

     2. A variety of methods of preparing and adding aluminum resinate were used.

        a. Fresh unfiltered aluminum resinate gave almost as good sizing (IV C) as the usual precipitation on all the fibers.

        b. None of the filtered mixtures were nearly as effective.

The following sheets all had aluminum resinate precipitated on a pulp portion, filtered.

			Currier	Tappi
VI.	H,	1.5% Alum	20.1	32.1
VI.	I,	2.25% Alum	12.4	18.8
VI.	F,	3% Alum	16.3	21.1
VI.	G,	3% Alum before Rosin	4.8	8.6
VI.	J,	4% Alum	12.8	20.5
VI.	K,	4% Alum + 1% NaOH	14.9	25.8
VI.	L,	6% Alum + 2% NaOH	30.0	39.6

It seems probable that in all these the pH of the small volume in which precipitation took place was too low to secure satisfactory alumina. In the presence of all the pulp, a greater proportion of the alumina and acid would be sorbed from the alum solution and raise the pH into the range 4.6 - 6.5 previously suggested as optimum.

3. In IV F and G, the additional alkali used was excessive, resulting in incomplete precipitation of the rosin, but in VI C the amount used was about right giving a nearly neutral sheet with a loss of 10% in size value.

4. In VI K and L procedures which should give a lot of alumina still failed to be very effective in the separate precipitation method.

Probably the real solution of this problem will involve the use of some such high-free-rosin size as the Bewoid size, as this involves little alkali to be neutralized and little electrolytes left in the sheet. The fresh Bewoid size obtained from Peterson was listed at 35% total solids and was diluted to 3% Bewoid size. Tables 3, 4, and 5 describe the results obtained by this material in various procedures.

Table 3. First Run with Bewoid Size

		pH	Basis Weight	Size Currier	Size Tappi
V. A, Pulp + 2% Na Resinate + 3% Alum		4.9	41.5	41.9	43.8
V. B, " + 2% Bewoid size + 1% "		6.5	42.1	43.6	44.7
V. C, " + " + 2% "		5.6	40.3	40.0	44.3
V. D, " + " + 3% "		4.6	42.0	43.4	45.3
V. E, Pulp + 2% Bewoid + [water + 3% Alum + 1% NaOH]		7.2	42.3	43.3	44.5
The alumina was not filtered but stirred into pulp + Bewoid					
V. F, Pulp + 2% Bewoid + [Pulp + 3% Alum + 1% NaOH, Filtered]		7.3	41.7	39.7	42.4
V. G, Pulp + 2% Bewoid + [Water + 3% Alum + 1.2% NaOH]		7.9	43.0	41.3	46.1
V. H, Pulp + " + [Pulp + 3% Alum + 1.2% NaOH Filtered]		7.6	41.4	36.1	39.1

My 3% alum is equivalent to 1.2% NaOH, while 0.9% NaOH was previously shown to give complete precipitation of the aluminum.

Table 4. Second Run with Bewoid Size

		pH	Basis Weight	Size Currier	Size Tappi
VII. A, Pulp + 2% Na Resinate + 3% Alum		4.7	42.7	48.8	49.7
VII. B, " + 2% Bewoid Size + 2% "		5.6	42.5	39.4	44.3
VII. C, " + " + 3% "		5.6	42.7	33.6	40.2
VII. D, " + 0.5% NaOH + 2% Bewoid + 3% Alum		8.0	41.6	25.0	33.0
VII. E, " + [water + 0.5% NaOH + 2% Bewoid + 3% Alum)		6.3	41.9	31.4	37.6
VII. F, " + [Pulp + 0.5% NaOH + 2% Bewoid + 3% Alum, Filter]		7.1	42.5	25.9	32.3
VII. G, " + 2% Bewoid + [Pulp + 3% Alum + 1% NaOH Filter]		7.1	43.7	42.9	49.5
VII. H, " + " + [Water + 3% Alum + 2% Na Resinate]		5.0	43.8	37.8	45.3

In F the turbid filtrate (pH 3.8) was too acid and contained aluminum. In G the clear filtrate (pH 7.2) contained no alumina. System D seems to be in error.

Table 5. Third Run with Bewoid Size

			pH	Basis Weight	Size Currier	Size Tappi
VIII.	A, Pulp + 2% Na Resinate + 3% Alum		4.9	44.0	43.6	46.8
VIII.	B, " + 2% Bewoid + 3% Alum		4.6	43.3	46.3	48.9
VIII.	C, " + " + [Water + 3% Alum + 1% NaOH]		7.3	42.7	40.7	42.8
VIII.	D, " + " + [Pulp + 3% Alum + 1% NaOH, filter]		7.5	43.5	43.6	44.1
VIII.	E, " + " + [Pulp + 3% Alum + 0.75% NaOH filter]		7.1	42.4	38.0	39.1
VIII.	F, " + " + [" + " + 1.5% "]		7.6	43.3	30.6	36.0
VIII.	G, " + " + 5 cc 5% H2SO4		6.5	42.9	2.9	7.7
VIII.	H, " + " + 5 cc 5% CaCl2		7.2	42.8	4.5	8.7

The filtrates and their pH values; D - 7.5 (slightly too alkaline), E - 4.8 (slightly too acid), F - 9.7 (much too alkaline.).

From these three runs with the Bewoid size, the following conclusions are drawn:

1. The Bewoid size appears about as effective as the sodium resinate. It appears that with either, no definite effect is demonstrated to depend upon the amount of alum used so long as the pH remains within the range 4.6 - 6.5.

2. Good sizing results (VIII C, V E, and G) from adding separately precipitated, but unfiltered, alumina to pulp Bewoid mixtures; but there is about a 10% loss in sizing if the alumina be precipitated on a portion of the pulp (V F and H), filtered, and the wet pad added to the rest of the pulp. However, VII D and VII G were excellent by this method.

3. In system V E - H inclusive, good sizing with Bewoid is demonstrated in alkaline systems - more alkaline than CaCO3 (pH 7.3).

4. This precipitation of the 95% free-rosin Bewoid size by the separately precipitated alumina practically completely precludes any possibility of the formation of aluminum resinate to effect sizing and yet is effective.

5. Neither sulphuric acid nor calcium chloride are effective in giving sizing with Bewoid.

The specific conclusions demonstrated by the data in the tables are detailed in the report. Certain general conclusions may be listed in summary:

1. While no procedure has been found superior to the usual rosin-alum addition to pulp, it is possible to obtain good sizing (IV C) by the addition of a fresh separately precipitated aluminum resinate to a pulp. In other words, it is not necessary to precipitate the sizing complex directly on the fibers.

2. Various procedures aimed at precipitating aluminum resinate on 10% of the total pulp to be used, filtration, and then mixing this pad with the rest of the pulp have failed to give more than about 75% of the sizing possible with the usual method. It should be possible to improve this.

3. The effect of amounts of alumina formed still appear as of less moment than the pH of the sizing systems.

4. By means of Bewoid size, it is possible to obtain good sizing by means of precipitated and filtered alumina. This is of interest as a major objective of the project. It throws light on the mechanism of sizing since little aluminum resinate can possibly be formed.

5. An important by-product of these data, and some to come, is that it is thus possible to secure well-sized sheets from alkaline suspensions. The results of the handsheets technic must be accepted with caution, but it appears possible that the methods here described (and some yet to be reported) will permit sizing of sheets left neutral or slightly on the alkaline side. This should be of interest not only for the carbonate-filled sheets (pH 7.3) but also possibly for closed water systems whose pH could be maintained throughout the cycle at any desired pH, the aluminum resinate or other form of size being separately precipitated and added to the pulp. This rests on the not yet completely proved assumption that good sizing depends primarily on the pH of the system in which the size was precipitated, and is but slightly influenced by not excessive contact with systems at other pH values.

hl

PROJECT REPORT FORM

Sizing with Fatty Soaps and Soap-Starch Mixtures.

FILED JUN 13 1938

The aluminum soaps of the fatty acids have long been used for waterproofing of textiles and many other articles and surfaces. In February, 1937, I suggested a trial of soap-alum sizing, and on March 23, 1937 (p. 41258) we carried out such a test on a mixed furnish of unbleached soda and unbleached sulphite pulps. The conclusions of that run were that sodium oleate is more effective than rosin, while Swift soap, sodium stearate or ammonium oleate are about as good as rosin. It is reported that at least one member organization is commercially sizing special papers by some such combinations.

At various times last year beginning January 11, 1937 (p. 41170) and continuing through a number of runs, it was suggested and demonstrated that starch mixed with soap could be completely precipitated by alum, but that rosin was without effect. The physical strength of the sheets produced showed disappointingly little improvement and the work was dropped.

It seemed worthwhile with the Weyerhaeuser bleached sulphite pulp being used for this work to give the thing another trial in an attempt to discover hitherto overlooked factors. The soap solutions used were old ones, made some months ago for the course. On standing, they appear to agglomerate, hydrolyze, etc., so that fresh solutions will probably work better. Even a heating just before use disperses the soap, and this was done for Series IX but not for Series X.

Table 1.   Sizing with Soap and Alum

		pH	Basis Weight	Size Currier	Size Tappi
IX.	A, Pulp + 2% Na Resinate + 3% Alum	4.8	48.9	58.0	55.5
IX.	B, Pulp + 1% Na Oleate + 3% Alum	4.7	48.7	46.2	47.7
IX.	C, Pulp + 2% Na Oleate + 3% Alum	4.9	48.3	51.8	49.7
IX.	D, Pulp + 4% Na Oleate + 3% Alum	5.5	47.3	21.3	27.6
IX.	E, Pulp + 1% Swift Soap + 3% Alum	4.7	47.4	22.5	30.1
IX.	F, Pulp + 2% Swift Soap + 3% Alum	4.7	48.3	45.5	47.0
IX.	G, Pulp + 1% NH$_4$Oleate + 3% Alum	4.7	47.6	36.8	42.7
IX.	H, Pulp + 2% NH$_4$ Oleate + 3% Alum	4.8	47.9	50.3	48.5

Table 2.   Sheets with Soap-Starch-Alum

		pH	Basis Weight	Size Currier	Size Tappi	Mullen pts. /100 lbs.
X. A, Pulp + 2% Na Resinate + 3% Alum		4.9	47.4	56.0	57.5	104
X. B, Pulp + [2% Na Resin + 4% Starch] + 3% Alum		4.9	45.9	55.5	54.9	122
X. C, Pulp + 2% Swift soap + 3% Alum		4.7	47.0	31.9	36.7	89
X. D, Pulp + [2% Swift Soap + 4% Starch] + 3% Alum		4.6	51.1	63.6	58.0	141
X. E, Pulp + 2% Na Oleate + 3% Alum		4.8	46.8	46.4	47.3	78
X. F, Pulp + [2% Na Oleate + 4% Starch] + 3% Alum		4.8	49.2	61.0	56.8	122
X. G, Pulp + [2% NH_4 Oleate + 4% Starch] + 3% Alum		4.7	49.8	60.8	57.0	130
X. H, Pulp + [Na_2 Silicate + 4% Starch] No Alum		9.8	44.4	Zero	Zero	116

For the preparation of Series X, Royal Tapioca Starch was dispersed by heating to 90° C. with stirring. Then 100 cc of this warm 2% starch dispersion was treated with one gram (20 cc 5% solution, etc.) of the soap and the whole diluted to 200 cc which was 1% with respect to starch and 0.5% with respect to soap -- 40 cc of the mixture being taken for each batch of sheets containing 10 g. O.D. pulp. In the systems duplicated in the two series (IX C and X E) (IX F and X C) the first sheets made show higher size than those made two days later. This is probably because the soap solutions were heated to clearness before the IX series, and were not so heated before the X series.

The following conclusions appear justified.

1. In each of the three soaps tested, 2% of the soap gives nearly as good sizing as 2% sodium resinate. One per cent additions of the soap give lower values while 4% sodium oleate is quite low.

2. Starch does not affect rosin sizing, but does give the usual strength gain. This agrees with the previous demonstration that rosin is not helpful in the precipitation of starch.

3. All three of the soaps used with starch give better sizing than rosin and two of them improve Mullen. Most noteworthy is the cheap Swift soap producing the highest size values in the set (or the project so far) and a remarkably high Mullen.

Sizing with Sodium Silicate. Merely to keep the record complete, it is to be noted that Series XI, in which an attempt was made to secure sizing by precipitation of sodium silicate by alum, proved to be a complete flop -- all the size tests being zeros. While it is true that the silicate was more alkaline than I anticipated, and the sheet pH values are too high to ensure complete precipitation of alumina and silica, there appears little promise in this direction. Whatever contribution silicate makes to a sheet of paper it does not appear to confer on it any water resistance.

Conclusions:

        1. Three soaps (sodium oleate, ammonium oleate and Swift soap) may be precipitated by alum, and produce nearly as good sizing as sodium resinate.

        2. One of the most interesting developments of this project so far is the finding that if these soaps be mixed with starch and precipitated by alum.

        a. The starch adds considerably to the sizing power of the soap -- nearly doubling it in the case of Swift soap, and thus exceeding the value for rosin.

        b. The soap adds considerably to the strength imparted by the starch.

	Mullen
Rosin - Alum	104
Rosin - Starch - Alum	122 - gain 18 pts.
Swift soap-starch-alum	141 - gain 37 pts.

        3. Dr. Rowland suggests today that this effect will probably be even more marked if applied to a pulp not beaten so far as this. This sulphite pulp was beaten to a freeness of 545 cc.

        4. Sodium silicate confers no sizing.

hl

PROJECT REPORT FORM

Solvent Sizing. Rosin Sizing Affected by Wetting Agents, Salt, Calcium and Magnesium Ions

Solvent Sizing. In the first report on this project, dated February 26, 1938, it was suggested that possibly a solvent sizing, employing aluminum resinate instead of the usual rosin, should have certain virtues if effective. A sample of aluminum resinate was prepared two months ago and qualitative tests showed that a benzene solution of it did render paper well-sized. This idea was continued in the work here reported.

Qualitative tests showed that the aluminum resinate is readily soluble in benzene, toluene, ethylene dichloride, chloroform, carbon tetrachloride (fairly). It is not apparently soluble in ethanol, kerosine, or acetone, cold or hot. In one of Minton's papers on solvent sizing, using rosin, he says that alcohol tends to dehydrate the fibers and that carbon tetrachloride or ethylene dichloride would probably be better. Ethylene dichloride (B.P. $83°$) was chosen because of its lower toxicity, flame hazards, and ability to dissolve both rosin and aluminum resinate. The paper dipped was the 100% rag stock from Fox River Paper Company, long used by Kjelson for starch coating. Pieces were cut 7-1-x inches x 6 inches weighing about 2 grams each. Nelio rosin was dissolved in ethylene dichloride; aluminum resinate was also dissolved in the same solvent. The sheets were drawn once through 100 cc of the solutions shown, contained in a special tray, previously used for such dips, and were then hung up. After eight sheets had thus been dipped, the last few were permitted to dry a few minutes and were then heated 5 minutes on the Williams drier. After use, 50 cc of the 2% aluminum resinate solution were diluted with 50 cc more of ethylene dichloride, called 1% solution and used for C and G. In similar fashion dilution gave solution for D and H.

Table 1. Solvent Sizing

		Size	
		Currier	Tappi
Blank - Untreated sheet		17.	21.0
XII. A, Dip in 1% Nelio Resin in Ethylene Dichloride		28.7	31.0
XII. B, Dip in 2% Aluminum Resinate in Ethylene Dichloride		32.6	35.5
XII. C, Dip in 1% Aluminum Resinate " " "		30.0	32.5
XII. D, " " 0.5% " " " " "		32.5	35.9
XII. E, Same as A, followed by heating in drier		30.7	34.3
XII. F, " " B, " " " " "		35.7	38.0
XII. G, " " C, " " " " "		35.9	38.2
XII. H, " " C, " " " " "		30.7	32.9

Conclusions from these data:

     1. All the aluminum resinate systems show better sizing than the rosin sizing.

     2. The one per cent solution is about as effective as 2% aluminum resinate.

     3. Heating the sheets on the drier brings in general a small increase in size.

Rosin Sizing in Presence of Wetting Agents and of Salt.

In connection with the recent work on the sizing problem at Escanaba, it appeared that some pulps might contain capillary active wetting agents which might prevent sizing, or by increasing the wetting by water give low size tests. It was shown by Reineck that the Soo pulp contained a material which could be extracted by washing and whose removal permitted good sizing of the Soo pulp. It was argued that the extracted material might inter-fere with the normal sizing of the Weyerhaeuser bleached sulphite pulp used in this work, and the explanation be thus complete. Reineck extracted 10 g. of Soo pulp with 300 cc water which was then added to our pulp, XIII B and a second extraction was used XIII C. Unfortunately neither of these showed any large effect on sizing. But the possibility still exists that a wetting agent left in a pulp might give low sizing values. A most likely impurity would be the lignosulfonic acids in the sulphite waste liquor if incompletely washed out. A fresh sample of sulphite liquor (pH 2.1) in the Interlake mill was used as shown - on 10 g. O.D. pulp batches. As a further check Sulfatex, a wetting agent in use by Phoenix and Duponel, were employed as a typical wetting agent such as might purposely be introduced by some mills.

Finally it has become somewhat of a legend among the practical men of the industry that chlorides ruin sizing, although nobody has any ideas as to the explanation. Typical of such comments is the statement attributed to Arnould (1921) to the effect that the presence of only 0.043% sodium chloride in a pulp may completely prevent sizing by the usual rosin-alum method. He suggests the mechanism may depend on the action of crystalloid sodium chloride on colloidal resin, which is true but not useful. Washing with water may be ineffective for the removal of the strongly sorbed salt, and dilute caustic followed by thorough washing must be resorted to. Since this figure means less than one tenth of a pound of salt per ton of stock, this should mean that no pulp in natural water would ever size. At any rate, systems XIII K and L demonstrate that ten and twenty times this much salt are still far from destroying sizing and probably this hazard has been grossly overrated.

Table 2. Sizing - Wetting Agents, Salt

				Basis	Size	
			pH	Weight	Currier	Tappi
XIII. A, Pulp + 2% Na Resinate + 3% Alum			4.8	46.1	44.3	47.1
XIII. B, " + 300 cc First Ext. Escanaba Pulp + 2% Na Resinate + 3% Alum			4.8	45.9	42.0	47.9
XIII. C, " + 300 cc Sec. Ext. + 2% Na Resinate + 3% Alum			4.9	45.3	47.7	44.3
XIII. D, " + 1% Duponal + 2% Na Resin. + 3% Alum			5.0	45.2	31.0	38.8
XIII. E, " + 2% " + 2% " + 3% "			5.1	45.2	Zero	Zero
XIII. F, " + 5 cc Sulphite Lig. " + "			4.6	45.0	40.3	46.7
XIII. G, " + 10 cc " " " + "			4.6	46.3	48.2	49.3
XIII. H, " + 20 cc " " " + "			4.4	43.4	26.9	33.2
XIII. I, " + 0.5% Sulfatex + " + "			4.9	42.7	29.7	35.5
XIII. J, " + 1% " + " + "			4.9	43.1	16.5	22.8
XIII. K, " + 0.5% NaCl + " + "			4.8	42.8	40.6	43.3
XIII. L, " + 1% NaCl + " + "			4.8	42.6	36.5	42.6

Conclusions:

1. The extract from the Soo Escanaba pulp has practically no influence here.

2. Both Duponol and Sulfatex do markedly decrease sizing. The zero values in E are too low to be accepted without confirmation.

3. Sulphite liquor in amounts up to 100% on the pulp have, if any, a slightly beneficial effect on sizing. These systems all gave excessive foaming, and floating of the pulp - the G being the worst as well as giving the best sizing. Excessive sulphite liquor reduces size.

4. Sodium chloride additions lower Currier size values somewhat - probably due to the same mechanism as previously advanced for sodium sulphate, the conductivity of the penetrating water. They have less effects on Tappi size. In neither case do these excessive amounts ruin sizing.

Sizing in Presence of Calcium and Magnesium

The most recent series run was designated to demonstrate the effect of hardness of water on sizing. While the run is not satisfactory in several respects and must be repeated, it seems to throw some light on the problem. The Appleton tap water runs about 150 p.p.m. in hardness reckoned as $CaCO_3$. The solubility of $CaCO_3$ is 0.00153 g./100 cc. a 15.3 p.p.m., while CO_2 increases this tenfold or more. Dr. Browning says that a very hard water might go up to 1000 p.p.m. (1 g./L), which in terms of $CaCO_3$(M.W. = 100) would be 0.01 M. The solutions used here were prepared by dissolving c.p. $CaCO_3$ and U.S.P. MgO in the calculated volumes of standardized acetic acid. Neither of the solids dissolved completely, and filtration was resorted to, so that the final concentrations are only approximately 0.4 M calcium or magnesium acetate. The acetate was chosen to avoid the then unknown effect of chlorides; the next time the chlorides may be used. In B and D, therefore, we have such concentrations of the salts as would be found in a tremendously hard water, while C and E contain four times this much hardness. The original calcium acetate had a pH of 5.2, while that of magnesium acetate was 5.3, both therefore representing an excess of acid, since the solutions should be nearly neutral or on the alkaline side. The pulp used had been beaten six days previous to the run. To ensure equilibrium the $CaCO_3$ (10% on pulp) was mixed with the pulp and allowed to stand overnight before size was added.

Table 3. Sizing in Presence of Calcium and Magnesium

			pH	Basis Weight	Size Currier	Tappi
XIV. A,	Pulp + 2% Na Resinate + 3% Alum		4.9	40.8	32.6	34.6
XIV. B,	Pulp + 0.01 M Ca Acet. + 2% Na Res. + 3% alum		5.4	41.0	33.5	34.8
XIV. C,	Pulp + 0.04 M " + " + "		5.3	40.0	29.9	31.9
XIV. D,	" + 0.01 M Mg. Acet.+ " + "		5.4	39.2	34.8	37.8
XIV. E,	" + 0.04 M " + " + "		5.4	44.6	49.9	43.7
XIV. F,	" +(0.01M Ca Acet. + " + "					
	(0.01M Mg Acet. + " + "		5.4	44.5	41.7	39.8
XIV. G,	" +(0.01M Ca Acet.					
	(0.01M Mg. Acet. + 3% Alum + 2% Na Res.		5.4	43.6	44.6	42.3
XIV. H,	" + 3% Alum + 2% Na Resinate		5.1	41.6	16.0	20.0
XIV. I,	" + 10% Ca CO$_3$ + 2% Na Res. + 3% Alum		7.3	44.2	5.0	9.2
XIV. J,	" + " + 3% Alum + 2% Na Res.		7.4	45.2	Zero	2.9
XIV. K,	" + " + [Pulp without CaCO$_3$ + 2% Na Res. + 3% Alum, no filter]		7.3	44.0	2.3	4.8
XIV. L,	" + " + [Water + 2% Na Res. + 3% Alum, no filter]		7.3	45.1	1.7	4.2

Conclusions:

1. Calcium decreases size but slightly even in these large amounts; magnesium very unexpectedly _increases_ sizing in every system where it is used, and up to 50% above the blank. In three cases of four magnesium gives Currier size above Tappi values, contrary to the usual finding. The higher basis weights of the magnesium sheets is complicating and requires repetition.

2. Adding alum before rosin gives an abnormally low value in H (previous IV E and VI B) runs showed only 10 and 20% loss in sizing), but does appear to improve sizing in hard water (cf F and G).

3. In no CaCO$_3$ system is there any sizing, and the reason for this must be sought further. It was argued that since a separately precipitated aluminum resinate gave good sizing when stirred into a pulp (even though the final pulp mixture be on the alkaline side), it should continue to do so even in the presence of CaCO$_3$ which buffers systems so that they can not go below about pH 7.3 in its presence. How calcium carbonate can affect precipitated aluminu m resinate is not clear, unless it forces a straight double decomposition reaction, or selectively adsorbs and agglomerates the sizing material. It should be possible to avoid this difficulty. Peterson achieves sizing of carbonate filled sheets by the use of Bewoid size precipitated by alum added at the fan pump (minimizing principle). The hardness of water consists chiefly of Ca and Mg chlorides and sulphates, and it may be that the use of such salt will have a greater effect than the acetates.

The general results of this report include:

     1. Solvent sizing using aluminum resinate in ethylene dichloride is more effective than such sizing with rosin. According to Dr. Kress, many unsuccessful efforts have been made to achieve solvent sizing (especially with the Minton equipment), so that it is a desired but yet unattained goal. It has the great virtue, pointed out by Minton, of introducing no electrolytes into the sheet and, if a solvent, recovery process can be worked out, would probably be welcomed. My idea is that such a process using <u>aluminum</u> <u>resinate</u> should show a greater resistance to aging than rosin alone.

     2. Wetting agents (sulfatex, Duponol) do lower size values.

     3. Sulfite waste liquor in moderate amounts has no great effect, but does increase foaming, and, in excess, reduces size.

     4. Sodium chloride additions have a slight effect on Tappi sizes; on Currier size they give lower values, probably attributable to the increased conductivity of the penetrating liquids. These large additions do not ruin sizing as is alleged for much smaller impurities of salt.

     5. Calcium or magnesium acetate exhibit no very severe influence on sizing even when used in much larger concentrations than would be found in hard water.

     6. Calcium carbonate still ruins sizing, even when the aluminum resinate is separately precipitated.

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I. Checking and Extending Runs on Separate Precipitation of Aluminum Resinate

In runs IV and VI reported previously, various methods were tried involving the separate precipitation of aluminum resinate without or with a portion of the pulp, and without or with filtration before the sheets were made. The run #15 was designed to investigate these procedures further. The materials enclosed in parentheses were mixed as shown before being added to the pulp.

TABLE I

SEPARATE PRECIPITATION OF ALUMINUM RESINATE

		pH	Basis Weight	Size Currier sec.	Tappi sec.
15A	Pulp + 2% Na Resinate + 3% Alum	5.1	43.6	35.6	42.1
15B	Pulp + (100 cc. tap water + 2% Na Resin. + 3% Alum)	5.2	44.1	41.0	42.3
15C	Pulp + (Water + 3% Alum + 2% Na Resin.)	5.3	43.5	29.0	30.7
15D	Pulp + (Water + 0.6% NaOH + 2% Na Resin. + 3% Alum)	7.1	43.4	34.5	35.6
15E	Pulp + (Water + 2% Na Resin. + 3% Alum + 0.6% NaOH)	7.1	43.0	20.4	29.8
15F	Pulp + 2% Na Resin. + 3% Alum + 0.25% NaOH	6.4	45.0	38.4	40.8
15G	Pulp + 2% Na Resin. + 3% Alum + 0.5% NaOH	6.8	44.7	37.1	41.0
15H	Pulp + (100 cc. Pulp + 2% Na Resin. + 3% Alum, no filter)	5.1	45.1	41.4	41.7
15I	Pulp + (100 cc. Pulp + 2% Na Resin. + 3% Alum, filtered)	7.5	44.0	9.8	15.5
15J	Pulp + (100 cc. Pulp + 2% Na Resin. + 3% Alum, + 0.5% NaOH, filtered)	7.3	45.0	18.7	27.0
15K	Pulp + (100 cc. Pulp + 2% Na Resin. + 3% Alum, + 0.75% NaOH, filtered)	7.3	44.7	23.4	32.7
15L	Pulp + 2% Na Resin. + 3% Alum + 1% NaOH	8.1	44.7	28.5	33.8

The following conclusions may be drawn from these data:

1. The separate precipitation of aluminum resinate in some water (B) and the addition of this fresh suspension to the pulp gives just about as good sizing as the usual precipitation in presence of fibers (A). This involves mixing the AlR₃ suspension (pH - 4.1) with the pulp suspension (pH - 8.1) to give a final system at pH - 5.1.

    a. But adding alum first in this method (C) is poor practice, and

b. Adding 0.6% NaOH before (D) or after (E) the rosin-alum loses size. The attempt here was to produce good sizing in neutral systems, and (D) gives good sizing at pH - 7.1, although slightly inferior to (A).

2. **Aluminum resinate** may also be **precipitated (H) on** about a tenth of the total **pulp** and then mixed with the rest of the pulp to give sizing as effective as if it were precipitated on all the pulp.

a. But if this system be filtered (I) (pH of filtrate 4.1) and the wet pulp pad be mixed with the rest of the pulp there results the poorest sizing here.

b. The addition of alkali (J, K) helps but does not cure this condition. The filtrates from (I) (pH - 4.1) and (J) (pH - 4.4) contained peptized alumina precipitated by ammonia or by standing over night, but the filtrate from (K) (pH - 6.7) was clear and contained no aluminum. It seems probable that pH - 7.3-7.5 is too high for effective sizing and could be brought to the acid side by acid addition to the original pulp in tap water (pH - 8.1) (tap water alone, pH - 7.5).

3. Following rosin-alum by 0.25% (F) or 0.5% (G) NaOH to pH - 6.4-6.8 is without effect, but 1% NaOH (L) to pH - 8.1 is excessive. This confirms the previously expressed opinion that good sizing would be possible in the pH range 4.6 - 6.5. The most promising development would be pulp brought to pH - 6-7 by acid and then treated as in (F) or (L) without or with filtration.

II. Sizing with Bewoid Size

The same dilution of Bewoid size was used as in series V, VII, and VIII. Standing five weeks caused the 3% Bewoid size to have a slightly bad protein odor, and on dilution with tap water it flocculates badly, although the undiluted sample smells satisfactory. When fresh the 3% Bewoid size is stable to tap water.

TABLE II

FOURTH RUN WITH BEWOID SIZE

		pH	Basis Weight	Size Currier sec.	Tappi sec.
16A	Pulp + 2% Na Resinate + 3% Alum	5.1	45.1	42.1	43.4
16B	Pulp + 2% Bewoid Size + 3% Alum	4.7	44.7	39.6	41.4
16C	Pulp + 2% Bewoid Size + 3% Alum + 0.5% NaOH	6.3	44.8	34.7	40.8
16D	Pulp + 2% Bewoid Size + 3% Alum + 1% NaOH	7.6	44.5	33.7	36.6
16E	Pulp + 2% Bewoid Size + (Water + 3% Alum + 0.5% NaOH, not filtered)	6.5	44.3	36.6	36.5

TABLE II (continued)

FOURTH RUN WITH BEWOID SIZE

		pH	Basis Weight	Size Currier sec.	Tappi sec.
16F	Pulp + 2% Bewoid Size + (Pulp + 3% Alum + 1% NaOH, filtered)	7.5 7.2	45.3 45.8	34.7 26.2	35.0 33.2
16G	Pulp + 1 g. CaCO₃ + 2% Bewoid + 3% Alum				
16H	Pulp + 1 g. CaCO₃ + 2% Bewoid + (Pulp (CaCO₃) + 3% Alum + 0.5% NaOH, filtered)	7.6	44.5	21.7	28.0

Conclusions from Table II:

1. Bewoid is about as effective (B) as sodium resinate (A) in the usual method.

    a. At higher pH values (by adding NaOH to 6.3 or 7.6) there is some loss in sizing, as is true also of rosin.

2. Separately precipitated alumina (Alum + NaOH), unfiltered (E) or precipitated on pulp (F) and filtered gives about 15% less sizing than does the usual procedure. This is the crux of Dr. Rowland's idea, and the method would possibly be more effective if the alkalinity of the pulp suspension were neutralized as by acid or flue gas.

3. Calcium carbonate (G, H) does seriously reduce sizing with Bewoid also, but does not lead to complete destruction of size as it does with rosin.

III. Solvent Sizing with Malinckrodt Aluminum Soaps

This run included solvent sizing, using benzene solutions of aluminum resinate recently received from Wilkens-Anderson, aluminum resinate made three months before by Davis, and the aluminum soaps indicated, received as samples from Malinckrodt. These include grades: M (Monoacid, Al (OH)₂ Stearate, $.22 lb.); D (Diacid, AlOH (St)₂, $.20 lb.); Fluffy (Same as D, most useful grade $.20); T (Triacid, Al(St)₃, $.21 lb.). Also a Malinckrodt sample of calcium stearate, $.20 lb. One gram portions of the soaps were treated with 99 cc. benzene. The W-A. aluminum resinate dissolved to give a clear solution, all the rest being very turbid and the aluminum soaps showing a Christensen effect color in the benzene. Sheets of the Kjelson rag paper as used for the previous run (XII) were dipped once through the special tray. All sheets were dried in the hood; four of each lot were then heated five minutes on the Williams drier.

TABLE III

SECOND SOLVENT SIZING RUN

		Size	
		Currier sec.	Tappi sec.
17A	1% Nelio Resin in Benzene	29.2	31.4
17B	Same + Heating	29.2	30.6
17C	1% Aluminum Resinate, W-A	27.6	31.5
17D	Same + Heating	30.4	31.9
17E	1% Aluminum Resinate, Davis	31.0	31.2
17F	Same + Heating	36.8	35.4
17G	1% Malinckrodt Al. St. M	40.4	30.3
17H	Same + Heating	40.4	30.5
17I	1% Malin. Al. St. D	41.4	30.5
17J	Same + Heating	44.1	30.7
17K	1% Malin. Al. St. Fluffy	46.4	31.0
17L	Same + Heating	43.4	31.0
17M	1% Malin. Al. St. T	26.9	27.7
17N	Same + Heating	34.0	29.2
17O	1% Malin. Calcium Stearate	36.4	31.7
17P	Same + Heating	36.8	31.8
Ser. XII	Blank Untreated Sheet	17.9	21.0

Conclusions from Table III:

1. Practically all the soaps are more effective than rosin here. Since rosin is commonly applied from a polar solvent like alcohol, it may not be quite fair to compare it in benzene. Also the greater cost of the soaps may not make interesting even the 50% increased sizing in (J) and (K).

2. In general, heating makes no difference; in aluminum resinates it improves somewhat.

3. The Davis aluminum resinate is slightly superior to that from Wilkens-Anderson.

4. The Tappi sizes in the whole series are remarkably constant, while the Currier sizes showing improvement exceed the Tappi values (reverse of usual order).

5. The order of excellence for these materials is:

    Aluminum Stearate D or Fluffy M (Best)
    Calcium Stearate
    Al Stearate T (Would be expected to be best)
    The Aluminum resinates
    Rosin (Poorest).

6. In view of the commercial difficulties of carrying out solvent sizing and solvent recovery, no further work is now planned on this feature. If it becomes practicable, it should give permanent electrolyte-free sheets. One other trial might

be run to demonstrate the real advantage of these aluminum resinates and other soaps.
One of the principal defects of solvent sizing with free rosin is its impermanence.
A selection of these sheets might be made up and the size values determined after
intervals of natural or artificial aging. The aluminum resinate sheets should demon-
strate superior resistance to aging which might justify reopening the whole question.
Minton's views as to the superiority of solvent sizing rest upon much the same basis
as impelled us to set up this project - strength and color maintenance, resistance to
aging, etc. I believe these aluminum salts represent an advance beyond Minton's ideas.

IV. The Soap - Starch Sheets.

In runs IX and X it was shown that commercial fatty acid soaps give good sizing, and
that in cooperation with starch, the starch increases the sizing conferred by the
soap, and the soap increases the Mullen advantage conferred by the starch. It was
thought that fresh warm soap solutions might be even more effective than the ones
used then. The starch and soap dispersions were used the same day they were made.
For the three systems shown in the parentheses, the soap and starch were mixed and
stood together 3 - 5 hours before use. The starch cook obtained had some lumps but
the strength values are of the same order as those found in the previous run.

TABLE IV

SOAP - STARCH SHEETS

		pH	Basis Weight	Size Currier	Tappi	Mullen pts/100#
18A	Pulp + 2% Na Resinate + 3% Alum	5.1	38.4	29.7	31.8	95
18B	Pulp + 2% Swift Soap + 3% Alum	4.8	39.6	28.0	30.4	98
18C	Pulp + 2% Swift Soap + 2% Alum	6.1	38.9	22.2	25.3	96
18D	Pulp + 2% Na Resinate + 4% Starch + 3% Alum	5.1	39.5	38.6	35.2	129
18E	Pulp + 2% Swift Soap + 4% Starch + 3% Alum	4.8	39.1	33.1	33.0	122
18F	Pulp + (2% Na Resinate + 4% Starch) + 3% Alum	5.0	39.5	34.6	33.5	129
18G	Pulp + (2% Swift Soap + 4% Starch) + 3% Alum	4.8	40.1	37.1	33.0	125
18H	Pulp + 2% NH₄ Oleate + 3% Alum	4.8	39.8	13.4	22.3	103
18I	Pulp + 2% NH₄ Oleate + 4% Starch + 3% Alum	4.7	39.7	32.8	33.7	134
18J	Pulp + (2% NH₄ Oleate + 4% Starch) + 3% Alum	4.8	39.7	36.1	33.7	143*
18K	Pulp + 2% Sodium Silicate + 3% Alum	5.3	39.0	0	0	95
18L	Pulp + 2.5% Sodium Silicate + 6% Alum	4.13	38.7	0	0	99

Conclusions from Table IV:

1. The use of 155 grams of the final 1% pulp suspension for each sheet

(instead of the previous 170 g.) gives basis weights nearer 40# and more consistent. The lower basis weights must be taken into account in comparisons, however.

2. Comparison of (A), (B), and (C) shows Swift Soap, like Rosin, requires the lower pH (4.8) with more alum to be effective, and is then equivalent to rosin in sizing.

3. Starch definitely aids sizing for all three soaps. It is here most effective with ammonium oleate, although previously Swift Soap was superior. Probably longer time of contact of starch - soap would be an advantage with the fatty soaps. It tends to raise Currier size above Tappi size.

*4. Starch in presence of ammonium oleate adds about 40% more Mullen (J - 143) than it does with rosin (D, F - 129).

5. Silicate, even though brought to a low pH by alum, has no sizing nor strength - affecting properties.

V. Effect of Wetting Agents, Calcium and Magnesium

It seemed wise to check the runs XIII and XIV made on these effects. In those runs the acetates of the Ca and Mg were used but since it was demonstrated that sodium chloride does not impair sizing, the chlorides were used in this run. The Deceresol is a very effective wetting agent, $1.00 a pound, from the American Cyanamide Company.

TABLE V

EFFECT OF WETTING AGENTS, CALCIUM, MAGNESIUM

		pH	Basis Weight	Size Currier	Size Tappi
19A	Pulp + 2% Na Resinate + 3% Alum	5.1	39.0	25.2	31.4
19B	Pulp + 1% Duponal + 2% Na Resin. + 3% Alum	5.3	39.1	20.0	27.3
19C	Pulp + 2% Duponal + 2% Na Resin. + 3% Alum	5.5	38.9	0	0
19D	Pulp + 1% Deceresol + 2% Na Resin. + 3% Alum	5.4	39.1	0	0
19E	Pulp + 0.5% Deceresol + 2% Na Resin. + 3% Alum	5.2	39.1	0	0
19F	Pulp + 2% CaCl₂ + 2% Na Resin. + 3% Alum	4.8	39.8	28.6	32.5
19G	Pulp + 4% CaCl₂ + 2% Na Resin. + 3% Alum	4.8	39.0	31.5	31.1
19H	Pulp + 2% MgCl₂ + 2% Na Resin. + 3% Alum	5.0	38.7	26.0	30.1
19I	Pulp + 4% MgCl₂ + 2% Na Resin. + 3% Alum	4.9	38.1	27.2	32.7
19J	Pulp + 2% CaCl₂ + 2% MgCl₂ + 2% Na Resin. + 3% Alum	4.8	38.4	26.1	30.4
19K	Pulp + 2% CaCl₂ + 2% MgCl₂ + 3% Alum + 2% Na Resin.	4.9	38.2	25.1	30.2
19L	Pulp + 1% CaCl₂ + 1% MgCl₂ + 3% Alum + 2% Na Resin.	5.7	37.4	23.7	28.2

2% Duponal - pH 8.6   2% Deceresol - pH 6.8
2% CaCl₂ - pH 6.7   2% MgCl₂ - pH 6.3

-7-

Conclusions from Table V:

1. One per cent Duponol has some effect (B) but 2% Duponol (C) or 0.5% and 1% Deceresol (E and D) ruin sizing. The systems with Duponol check those of series XIII (D and E), while the Deceresol demonstrates its more powerful wetting action. The quantities shown are all reckoned on the weight of the pulp. One per cent reagent means 0.1 g. in one liter or a 0.01% solution in the original sizing beaker. Enough of these reagents is adsorbed on the pulp and held through the dilution in the mold and the drainage to ruin the sizing of the resultant sheets.

2. Neither calcium nor magnesium chlorides have any demonstrable effect on sizing. In run XIV it appeared that magnesium acetate had a favorable effect to increase size more than was to be explained by the higher basis weight, but that is not borne out in the present run. This lack of influence of $CaCl_2$ agrees with the statement of Sutermeister who believed $CaSO_4$ also harmless but recognized $CaCO_3$ and $Ca(OH)_2$ as extremely injurious. At first sight this would appear to be a matter of the high pH of the latter two. More work is in progress on this point, in the hope that a successful method of sizing carbonate-filled sheets may be found. At any rate, the hardness of water does not appear to be an important factor in reducing sizing.

3. Since there was no deleterious effect of calcium and magnesium, adding alum before rosin (K and L) gave no improvement. Therefore, if in the mill adding alum first does give an advantage, it must be for some other reason than to take care of the hardness of the water. Possibly the lowering of a high pH may be the real purpose and may be better achieved, as Dr. Rowland has demonstrated, by _acid_ addition.

4. The 2% $CaCl_2$ / pulp would be 0.2 g. per liter or 200 parts per million in the sizing solution. This is to be compared to the 150 p.p.m. hardness in Appleton water. In view of (L) another run will be made using smaller quantities of these salts left in contact with the pulp longer times. But it does not appear that calcium and magnesium ions in solution in the beater have any great effect on sizing.

Summary of This Report.

1. Not included in this report was any mention of some incidental observations to the effect that excessive agitation might cause 500 cc. (1.6% pulp) suspension to increase in volume by 150 cc. due to entrapped air when 20 cc. of sulfite liquor was added. This foaming action was discussed with Professor Heuser as an explanation of the floating of pulp sheets in the mercerizing bath in the viscose process, but does not appear a sufficient explanation. It did demonstrate an error introduced in hand sheet technics, if the pulp be taken out by _volume_ rather than by weight. p. 46346.

2. Some preliminary experiments on the mechanism by which calcium carbonate ruins sizing were also not detailed because they are inconclusive. They demonstrate that while the pH of $CaCO_3$ suspension is about 8.2 - 8.3, the addition of HCl (probably alum would work the same way) is followed by a drop in pH to 6 or 5 and then a gradual rise, the reaction with the solid being slow. This, of course, is the reason why the minimizing principle is effective; the water is drained away before the pH rises to excessive values. By the same token, the carbonate filler will finally bring the sheet on the alkaline side, ensuring its permanence.

3. Run #15 demonstrates again that it is not necessary to precipitate aluminum resinate on the fibers to get good sizing. Equally effective is a separate precipitation in water or on a pulp portion and then adding the whole to the pulp suspension.

a. But filtration of the pulp, AlR$_3$, and adding of the wet pad to the rest of the pulp is not effective. This is for one or both these reasons.

1. The precipitation system is at pH 4.1, too low to precipitate the alumina, so that much of it goes into the filtrate and spontaneously precipitates on standing. If the filtrate is not discarded, mixing of the whole at pH 4.1 with the pulp suspension at 8.1 brings the final pH to 5.1, a satisfactory sizing value. When the filtrate is discarded the final pH is 7.5 which is too high.

2. There is some component in the filtrate producing good sizing. This is probably colloidal alumina. Added alkali helps to precipitate it but does not entirely correct the trouble. More experiments on this will be done.

4. The Bewoid size can be precipitated by alumina separately precipitated on a pulp portion and yields about 15% lower size than does the usual method. This would give a sheet very low in electrolytes as proposed, and can probably be improved. Calcium carbonate reduces but does not ruin sizing with Bewoid size.

5. The Malinckrodt aluminum stearate D in benzene gave best results in **solvent** sizing – about 50% higher Currier values than rosin in aluminum resinate. The M grade and the calcium stearate were also effective.

6. Again it is demonstrated that fatty soap helps starch to raise Mullen, and starch helps soap to give good sizing. Starch in presence of ammonium oleate adds about 40% more Mullen than it does when used with rosin. It might be that Swift and Company or one of the other soap people might be willing to sponsor a program of research on this or related matters.

7. It is shown that 2% Duponol or 0.5% Deceresol on the pulp are able to ruin rosin sizing completely. This may some day have application to the use of such wetting agents in pulp or the prevention of such use.

8. Calcium or magnesium salts do not have the deleterious effect on sizing commonly imputed to the hardness of water. It seems doubtful if sizing is greatly affected by hardness and much more likely that the pH of such water is far more significant.

More detailed conclusions are drawn under each table for the data presented therein.

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PROJECT REPORT FORM

Aluminum Soaps as Sizing Agents

Some time ago some runs were made in an effort to introduce prepared aluminum soaps into the sheet. The first idea was to disperse the technical fluffy aluminum stearate (monobasic) from Malinckrodt by means of dispersing agents in water. No great success was achieved, although Deceresol and Igepon T gave fair results, with Ultrawet showing some effectiveness. Poor results here plus the consideration that, even if these were effective, the wetting agents would be likely to spoil sizing in the sheet led to the setting aside of this idea.

Another possibility would be to dissolve the aluminum soaps in an organic solvent and add this solution to the beater in the hope that the precipitated soap might be sorbed on the fiber before agglomeration proceeded too far. One gram of aluminum resinate from Wilkins-Anderson dissolves in 3 cc. benzene or ethylene dichloride, or in 3.7 cc. dioxan. Such solutions were dumped with rapid stirring into 200 cc. of 1.5 % pulp and sheets made as usual. The excessive amounts of soap collected in huge amounts, but the sheets appeared: dioxan- hard sized, benzene- well sized, ethylene dichloride-very little sizing. Since this represented 10 - 50 times the necessary amount of aluminum resinate, a repitition with a possible amount was indicated.

This was run with a freshly beaten (freeness 420 cc.) bleached sulfite Weyerhaueser pulp. The first five systems were designed to test the sizing efficiency of aluminum chloride and of lanthanum nitrate recently received from Lindsay Light and Chemical Company. (Dr. McCoy)

		pH	Basis Wt.	Currier Size	TAPPI
20 A	Pulp + 2 % Na Resinate + 3 % Alum	5.0	42.5	28.0	42.4
20 B	Pulp + 2 % Na Resinate + 1.8% La(NO$_3$)$_3$	6.8	42.6	22.4	38.8
20 C	Pulp + 2 % Na Resinate + 5.4 % "	5.8	43.4	27.1	40.9
20 D	Pulp + 2 % Na Resinate + 9 % La (NO$_3$)$_3$	5.6	43.6	31.7	40.4
20 E	Pulp + 2 % Na Resinate + 1 cc. AlCl$_3$	6.6	42.5	36.2	43.3
20 F	Pulp + 2 % Na Resinate + 3 cc. AlCl$_3$	4.8	43.9	38.4	44.7
20 G	Pulp + 2 % Al Resinate in Benzene	7.0	43.6	1.0	4.8
20 H	Pulp + 5 % Al Resinate in Benzene	7.0	43.7	3.5	8.8
20 I	Pulp + 2 % Al Resinate in Dioxan	7.3	43.4	2.0	8.8
20 J	Pulp + 4 % Al Resinate in Dioxan	7.3	43.7	3.5	10.3

(System 20 H showed lots of agglomerated soap aggregates.)

Conclusions:

1. The introduction of prepared aluminum soaps, either dispersed by wetting agents, or dissolved in organic solvents, does not appear very promising.

    a. Rapid precipitation may have allowed too little time for distribbution and sorption before flocculation occurred.

    b. A solvent more miscible with water might work better.

    c. Polar substances such as oleic acid might inhibit flocculation of the aluminum resinate.

2. Lanthanum nitrate is effective in giving sizing with rosin, and gives values comparable to those obtained with alum.

3. Aluminum chloride appears more effective than alum in sizing at a higher pH.

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PROJECT REPORT FORM

PROJECT NO._____ ‿ ‿ ‿
COOPERATOR_____Institute_____
REPORT NO._____12_____
DATE_____January 16, 1939_____
NOTE BOOK_____155_____
PAGE 46383_____TO_____46385_____
SIGNED_____Herbert L. Davis_____
H. L. Davis

Dehydration Phenomena in Starch Sols.

In November, Dr. Rowland and Dr. Davis discussed the work on starch then current, and evolved an attack which is here recorded. A long time ago Dr. Rowland observed that a sheet produced by precipitating starch on pulp fibers by alcohol addition, possessed enormous strength, and that the disintegration of such a sheet gave a pulp which could again be made into a very strong sheet. This suggested that dehydration of starch by alcohol or by some other method might give products capable if imparting remarkable properties to paper. Some of the students in the Colloid Course had shown that alcohol additions to starch sols produced precipitation of the starch unless alkali was added to increase the weak negative charge on the starch. This showed that in ordinary aqueous sols the stability of starch is due almost solely to its hydration, and that the charge is too slight to stabilize it, if this hydration be removed.

Certain questions arise as a result of this and subsequent work.

1. Would the alcohol on the pulp alone have produced any such effect of strength, or did the improvement depend on the starch?

2. Would it be possible to treat cellulose so that it does behave as starch with such dehydration procedures?

3. Is such an effect on starch reversible or irreversible?

4. Is there any possibility of commercial utilization?

5. Would other dehydration mechanisms prove cheaper and more effective? Materials to be considered here include Acetone, Ethanol, methanol at 6 cents per pound, glycerin at 17 cents for C.P. or 8-10 cents per pound for commercial grades.

The original idea was to bring the starch sol nearly to its flocculation point by the non-solvent, and then complete the precipitation with alum, added late in the papermaking process. If the starch dehydration be irreversible, the starch paste cooked in concentrated form, could be treated with alcohol, dumped in the beater, and finally precipitated by alum after the jordan. Probably the alkali-alum treatment would have significance here. The preliminary experiments do not make success, by such a simple procedure, appear very probable, but there is a real chance that other techniques may be more effective.

Some preliminary experiments performed at that time indicate that 10 cc. of 5 per cent Royal Tapioca starch required just about 3 cc. of Acetone

or 3 cc. of ethyl alcohol for complete precipitation. Dilution showed
that 10 cc. of 1 per cent Tapioca starch required 4 cc. acetone and that
addition of small amounts of alum does improve precipitation in systems
containing nearly the critical volumes of organic liquid. A sample of
oxidized starch "Starch Superfilm No. 4, Received 4/5/37" behaved similarly,
requiring slightly more acetone and being more affected by alum.

Ten cc. 25 per cent Superfilm starch required 4+ cc. acetone, and was
precipitated by 3 cc. acetone plus 7 drops 6 per cent alum. Diluted to
5 per cent starch, 10 cc. required 5+ cc. acetone or 3 cc. acetone plus
6 drops alum.

Conclusions:

    1. It is possible to precipitate ordinary Tapioca starch or an
oxidized starch by alcohol or acetone additions.

    2. The presence or subsequent addition of small amounts of alum
facilitate this precipitation by non-solvent liquids.

    3. A further investigation of these phenomena seems advisable, but
at present the amounts of organic liquids required to produce precipi-
tation appears excessive from the standpoint of a commercial application.
Thus in the tapioca starch run, 0.5 g. starch requires about five times
this weight of alcohol or acetone.

    4. No technic has been applied to test the reversibility of this
precipitation, and probably handsheet tests will be the most significant
criterion.

    5. In view of the known precipitating effects of 10 per cent soap
on the basis of starch, some other substances or methods will be sought
to be correspondingly effective. The tannin-starch effects described by
Dr. Koets suggests similar tests with related compounds.

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PROJECT REPORT FORM

PROJECT NO. _____ 578 /
COOPERATOR ____ Institute
REPORT NO. _____ 12
DATE _____ June 2, 1939
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PAGE 46432 TO 46434
SIGNED _Herbert L. Davis_
Herbert L. Davis

MODIFICATION OF PROSIZE

It was recently reported that the increasing adoptions of the prosize method of sizing is already using about a third of the national production of boric acid, and that the concern of the producers of boric acid, coupled with a good probability of an increased price on that material, create something of a problem. Dr. Rowland suggested a brief investigation of the process, especially with a view to the feasibility of replacing boric acid by cheaper and more abundant acidic materials. This report of a few experiments carried out this week (1) advances certain considerations of the preparation and properties of prosize, (2) outlines experimental results which make it appear that such materials as ammonium chloride or ammonium sulfate, or possibly carbon dioxide may effectively displace boric acid in the present procedure, and (3) suggests criteria and standards by which suitable prosize combinations and procedures may be evaluated.

The Rowland patent 2,116,768, issued a year ago, describes a procedure whereby a rosin size containing a slight excess of free rosin is treated with a protein such as milk casein or soy protein so that the protein is dispersed by alkali sorbed from the sodium resinate equilibrium. This hydrolysis equilibrium is still further displaced in favor of the free rosin acid by the addition of boric acid. The resultant very fine dispersion of free rosin is stabilized by the soy protein and some sodium resinate, so that alum addition results in the precipitation of a well distributed rosin size of superior effectiveness. Last December Mr. Engstrom reported their procedure was to start with a 70-80 per cent saponified rosin at 3 per cent rosin concentration, pH 9.45. Addition of 15 per cent soy protein on basis of rosin lowered pH to 9.35, and then addition of 15 per cent boric acid on basis of rosin lowered the pH to 8.8-8.85 which was then used as such. For experimental purposes, it appeared wise to start with a completely saponified rosin, and Dr. Rowland frequently advises addition of alkali to commercial size in order to start with the finest dispersion possible.

For the experiments described here, the completely saponified Nelio resin was used in the 3.12 per cent rosin concentration (0.1 M sodium resinate). The soy protein was weighed out (15 per cent on the basis of rosin used), soaked briefly in a little water, mixed with the sodium resinate solution and heated on the hot plate up to 70-80° C., with stirring. It appears probable that 60° C. would be a more satisfactory maximum temperature. Portions of the rosin-protein mixture so prepared were mixed with various dissolved acidic materials as shown below.

TABLE I

		pH	Appearance
A.	50 cc. 3.12 per cent Prosize Blank	9.4	Clear, yellow brown
B.	Same + 15 per cent Boric Acid	8.9	Milky
C.	Same + 15 per cent Sodium Bicarbonate	9.2	Slightly clearer than A.
D.	Same + 64 per cent Sodium Bicarbonate	9.0	Yellow milky, about as B.
E.	Same + 64 per cent Alum	---	Gelatinous flocculation
F.	Same + 50 per cent Ammonium Chloride	7.9	White milky, considerable precipitation.

A second lot gave the systems below:

		pH	Appearance
G.	50 cc. 3.12 per cent Prosize Blank	9.4	As A.
H.	Same + 2.5 cc. 10% NaHCO$_3$ (16%)	9.2	Slightly cleared
I.	Same + 5 " " " (32%)	9.1	Slight milkiness
J.	Same + 2.5 " " NH$_4$Cl (16%)	8.6	White milky
K.	Same + 2.5 " " (NH$_4$)$_2$SO$_4$ (16%)	8.8	White milky (less than J)
L.	Same + 2.5 " 6% Alum	9.2	Largely precipitated

A third batch was prepared using a new sample of sodium resinate:

TABLE II

		pH	Appearance
I.	50 cc. 3.12% Prosize Blank	9.7	Clear solution
II.	Same + 13% NH$_4$Cl	8.9	Yellowish milky
III.	Same + 25% " "	8.6	White milk
IV.	Same + 38% " "	8.4	White milk
V.	Same + 13% (NH$_4$)$_2$SO$_4$	9.0	Yellowish, pale milk
VI.	Same + 25% " "	8.8	White milk
VII.	Same + 38% " "	8.6	White milk
VIII.	Same + 1 cc. N HCl	9.2	Curds below clear yellow liquid
IX.	Same + 2 cc. " "	8.9	Stirred, curds and turbid "
X.	Same + 1 cc. N Acetic Acid	9.2	Same as IX.
XI.	Tube A + CO$_2$ gas 1 hour	7.3	White milk
XII.	Tube G + " " 1/2 "	7.8	White milk

In all the white milky systems, including the boric acid one, there was considerable precipitation of a white caky material.

It had been previously observed that the soy protein confers on the wax emulsion and on the prosize perfect resistance to flocculation even though extensively diluted with tap water. The microscopic examination of such dispersion is possible only after extensive dilution, and their use in the beater involves such dilution in tap water. The white milky systems obtained above were diluted by adding 50 cc. tap water to 1 cc. of the 3.12 per cent prosize combinations. This is still more concentrated (0.06 per cent) than the prosize would be after addition to the beater, but it does permit the dark field ultramicroscopic examinations recorded in Table III.

TABLE III

DILUTION SYSTEMS (0.06% Rosin in Prosize).

				Turbidity	Dark Field Appearance
A.	Prosize Blank	+ 1 hour CO_2		3	Excellent, 0.5 micron, fairly uniform.
B.	"	"	+ 15% Boric Acid	1 (Least)	Good, considerable larger particles.
G.	"	"	+ 1/2 hour CO_2	2	---
J.	"	"	+ 16% NH_4 Cl	3	Excellent, very few layer particles pH 8.2
K.	"	"	+ 16% $(NH_4)_2SO_4$	3	Excellent, more aggregates than J.
III.	"	"	+ 25% NH_4 Cl	2	---
IV.	"	"	+ 38% " "	4	Good, but lots of aggregates pH 8.3
VI.	"	"	+ 25% $(NH_4)_2SO_4$	1 (Least)	---
VII.	"	"	+ 38% " "	3	Fair, lots of aggregates-- protein?
XIV.	1 cc. 3.12% Sodium Resinate + 50 cc. tap water			-	Immediate flocculation pH 8.7

Systems without Protein

XV.	50 cc. 3.12% Sodium Resinate + 25% NH_4 Cl		pH 8.8
XVI.	50 cc. 3.12% Sodium Resinate + 38% $(NH_4)_2SO_4$		pH 8.9

Both of these systems were initially white milky dispersions but soon began to appear more and more yellowish and to deposit increasing amounts of rosin. One cc. portions of the fresh white dispersions were diluted:

1 cc. XV. + 50 cc. tap water	pH 8.8
1 cc. XVI + 50 cc. tap water	pH 8.7

These initially appeared fine and uniform dispersions, but gradually creamed downward and deposited rosin.

The pH values of some relevant systems were:

Distilled water 6.2   10% $NaHCO_3$ 8.0
Tap water   7.3   10% NH_4Cl 5.5
3.12% Na Resin 11.1 (est.) 10% $(NH_4)_2SO_4$ 5.2

CRITERIA FOR JUDGING PROSIZE PREPARATIONS

In the evaluation of these results for laboratory purposes, the following criteria seem justified on the basis of our emulsion experience. The correlation with practical mill results is the final test, but these are suggested tentatively.

A. Color. If the final prosize product is a dispersion of free rosin particles of the finest possible sizes, this dispersion will probably appear white. Insufficient acidic material (systems C, H, I, D with bicarbonate, or V with $(NH_4)_2SO_4$) develop increasing turbidity but the residual ionic rosin leaves the resultant system yellowish in color. In like manner, conditions under which the agglomerated rosin particles can continue to grow as in the absence of protective protein (systems XV and XVI) will develop a yellowish color. This agrees with the general colloid ideas of maximum scattering of light from particles in the zone of optimum colloidality.

B. Resistance to flocculation by the salts in hard water. As indicated above, this protective action is due to the protein. In the absence of protein, dilution with tap water flocculates saponified rosin, and this is an effect of the ions present, for the pH (system XIV) is higher than which would otherwise precipitate any rosin. It appears that this may well be one of the prime advantages of prosize to which it owes its commercial values; when ordinary rosin size is diluted in the beater it is probably extensively flocculated. If these flocs are sorbed on fibers immediately little harm is done, but if they agglomerate in the solution phase, covering power and sizing may be poor. On the other hand, prosize is not thus flocculated on dilution alone but waits for the alum addition to set it on the fibers in the best degree of dispersion. Satisfactory prosize preparations must, therefore, be capable of producing homogeneous, stable dispersions at dilution of 0.05 per cent rosin or less in ordinary tap water.

C. Ultramicroscopic appearance. For all such dispersions as these, direct observation will be a rapid check on methods and ingredients. Any good prosize preparation will have essentially all its rosin dispersed in particles one micron and smaller. These exhibit rapid Brownian movement and show no great tendency to agglomerate. There should be few if any particles of protein or rosin larger than this size.

CONCLUSIONS

1. Contrary to my first expectation, sodium bicarbonate is not very effective in reducing the pH of the rosin-protein systems. In view of the pH 8.0 for the 10per cent $NaHCO_3$ this is not surprising. Even though this salt costs only about two cents per pound, and although excess of it could do no great harm (except to require a lot of alum and produce CO_2) its use does not promise much.

	pH
A. 3.12% Na Resinate	11.1
B. Rosin + protein	9.4- 9.7
C. " " + 16% $NaHCO_3$	9.2
D. " " + 32% "	9.1
E. " " + 64% "	9.0

2. Small additions of hydrochloric or acetic acids or alum produced flocculations even through the pH was now lowered greatly.

3. The most promising compounds tried so far appear to be ammonium chloride or ammonium sulfate. Ammonium chloride technical costs nine cents but sal ammoniac white costs about five cents per pound. Ammonium sulfate (fertilizer grade) costs 1.4 cents per pound and a satisfactory material ought not to cost more than 2-3 cents.

4. Bubbling carbon dioxide through rosin-protein systems gives good prosize systems. These would be low in electrolytes. Flue gas might serve as a source of CO_2. The gas would probably have to be put in under pressure somewhat as Spencer does for his special alumina.

5. In order to achieve the milky white systems, the pH of the prosize must be lowered to or below pH 8.9. No lower limit has been ascertained. System XI (CO_2 for one hour) gave 7.3 as the lowest here recorded. The lower the pH, the lower the alum requirement—having in mind the alumina necessary to stabilize the size.

6. Suggestions for future work.

    a. Seek for improved protective colloids—glue, gums, etc.

    b. Try out other acidic materials.
       (1). Acids are cheap, if some method of introduction be devised.

    c. Investigate alum flocculation of prosize as affected by such variables.

PROJECT REPORT FORM

THE PRECIPITATION OF STARCH-SOAP COMPLEXES

In the previous report, "Dehydration Phenomena in Starch Sols," it was shown that alcohol or acetone precipitate starch from aqueous suspensions, and experiments were anticipated to discover other methods of dehydration. The performance of these experiments led to a disappointing lack of effectiveness of the substances added to the starch, so that it seemed wise to review the previous effective use of soaps for this purpose in order to ascertain the amounts required and the conditions of precipitation.

Varying Soap Additions

Since Heald has shown stearates to have greater effect than oleates, sodium stearate was used on Royal Tapioca starch. The starch suspension (2%) was cooked directly on the hot plate with good stirring to 90° C. Then 50 cc. of the 2% starch were mixed with appropriate volumes of hot 1% sodium stearate solution and the mixture diluted to 500 cc. of a solution 0.2% starch and 0.01, 0.02, 0.04% sodium stearate-- that is, 5, 10, and 20% soap on the basis of the starch. Only the significant systems in each run are reported. For each test 50 cc. of the 0.2% starch + soap mixture were treated with alum as shown. Final observations were taken after the tubes stood overnight.

TABLE I

	pH	Precipitate cm.	Appearance	
5% Sodium Stearate				
50 cc. (0.2% Tapioca + 0.01% Soap)	6.97	1.3	Turbid	
Same as above + 2.5 cc. 0.1% Alum	5.70	3.0	Nearly clear	All gave slight pur-
Same as above + 3 cc. 0.1% Alum	5.08	3.7	Clear	pled color
Same as above + 10 cc. 1% Alum	3.88	2.8	Clear	with iodine

TABLE I (Concluded)

	pH	Precipitate cm.	Appearance
10% Sodium Stearate			
50 cc. (0.2% Tapioca + 0.02% Soap)	7.04	0.8	Turbid
Same as above + 3 cc. 0.1% Alum	5.43	3.8	Nearly clear Slight iodine color
Same as above + 4 cc. 0.1% Alum	4.77	3.9	Clear No iodine color
Same as above + 20 cc. 0.1% Alum	3.79	3.2	Clear No iodine color
20% Sodium Stearate			
50 cc. (0.2% Tapioca + 0.04% Soap)	8.34	0.5	Turbid
Same as above + 4 cc. 0.1% Alum	6.14	1.8	Still turbid
Same as above + 0.7 cc. 1% Alum	4.35	4.5	Clear No iodine color
Same as above + 10 cc. 1% Alum	3.74	3.5	Clear No iodine color

Precipitation by Substances Other Than Alum

The data in Table I indicate that while 5% soap on the basis of the starch is insufficient, 10 or 20% soap enables alum completely to precipitate starch at pH values at or below 5. It was next sought to discover if other substances could precipitate the soap-starch complex. Using the same technic of adding soap to the cold starch, sulfuric acid was as effective as alum but calcium chloride and aluminum chloride failed to precipitate the complex completely. This was corrected when solid sodium stearate was added to the hot 2% starch sol.

TABLE II

Tapioca + 10% Sodium Stearate + $AlCl_3$, $CaCl_2$, H_2SO_4

	pH	Precipitate cm.	Appearance
50 cc. (0.2% Tapioca + 0.02% Soap)	7.02	-	Turbid
Same as above + 2 cc. $AlCl_3$	6.33	6.7	Slightly turbid
Same as above + 3 cc. $AlCl_3$	4.55	5.5	Clear No iodine color
Same as above + 10 cc. $AlCl_3$	4.37	5.5	Clear No iodine color
Same as above + 0.25 cc. $\underline{N}$ $CaCl_2$	6.45	10.7	All clear supernatant liquids, but all give
Same as above + 5 cc. $\underline{N}$ $CaCl_2$	6.50	5.8	slight purplish color with iodine.
Same as above + 0.75 cc. 0.1% H_2SO_4	6.13	12.0	Slightly turbid
Same as above + 0.85 cc. 0.1% H_2SO_4	6.18	5.4	Clear No iodine color
Same as above + 2 cc. 0.1% H_2SO_4	3.4	4.2	Clear No iodine color

Finally, duplicate runs were made which showed that there is no marked difference in the precipitation when starch was cooked in distilled or in tap water. In either case the dilution from 2% to 0.2% starch must be done in distilled water as otherwise the hardness of the tap water does precipitate the dilute starch-soap complex partially.

The general conclusions of this work are:

1. Five per cent sodium stearate on the basis of tapioca starch is inadequate, but 10 or 20% soap permits complete precipitation by alum when the pH reaches 5 or below.

2. The soap-starch complex may be precipitated also completely by aluminum chloride at about pH 5, by sulfuric acid at about pH 6, and partially by calcium chloride at pH 6.5.

3. Tap water is satisfactory to cook the starch in, but dilution of the starch-soap complex with tap water leads to its partial precipitation, which in the presence of fibers would take place on the fibers.

A STUDY ABOUT THE PREPARATION OF ALUMINA SOLS FROM ALUM

INTRODUCTION

The two principal methods of preparing alumina sols are the hydrolysis
of certain aluminum salts, especially of aluminum acetate, and the
peptization of gelatinous aluminum oxide with salts, usually aluminum
chloride, or with acids such as hydrochloric or acetic acid. In the
peptization method aluminum chloride used to be the starting material
from which a precipitate of alumina was obtained; this could then easily
be peptized to a stable and active sol. In a recent study, alumina sols
proved to be effective in the purification of water and future research
work in the Institute will deal with their use in the process of sizing
paper. Therefore, a further investigation of the preparation and properties
of alumina sols is not only of an academic interest but also of the greatest
practical importance. The first step in this extensive program aims at
the preparation of an active alumina sol from aluminum sulfate, the
papermaker's alum, which is consumed in large quantities by the paper
industry and which costs much less than aluminum chloride.

The very nature of alum, however, adds another factor to those already
present and complicates the preparation of a satisfactory sol. The divalent
negative sulfate ions unfavorably affect the charge and the zeta-potential
on the positive alumina micelles and consequently the stability and
reactivity of the sol. Such a phenomenon which had frequently been observed
lets the suggestion arise whether the method may be improved by a quick
and thorough removal of the disturbing sulfate ions from the system before
they fully exert their harmful influence. In this study most experiments
were based on such an assumption. Besides the effect of the anions many
other factors come into play and determine the final properties of the
sol. Among them there are the kind of precipitating reagent, its con-
centration and mainly that of the alum, the rate of adding the precipitating
reagent, the rate of stirring, the temperature, the pH value, and above
all the aging of the precipitated alumina, and probably a good many other
variables which are partly not yet known.

EXPERIMENTAL

The precipitation of alumina was done by adding a solution of ammonium

hydroxide or of sodium carbonate to a solution of alum. The Waring
Blender proved to be a very effective stirring device. A quick separation
of the precipitate from the liquid was brought about in the ordinary
centrifuge (about 3000 r.p.m.) or in Sharples Supercentrifuge (about
25000 r.p.m.). The sediment was repeatedly washed and centrifuged until
the test for sulfate ions with $BaCl_2$ was negative, which generally occurred
after the fifth or sixth run. In some experiments the precipitate of
alumina was allowed to settle without the application of the multiple
gravitational force of a centrifuge. Then the sediment was taken up
with water and the peptizing agent, mostly a one per cent $AlCl_3 \cdot 6H_2O$
solution, was added. Generally it was necessary to heat the suspension
on a hot plate to around 70° C. or to stir it in the Waring Blender in
order to obtain a better dispersion. In all experiments distilled water
was used.

According to the instructions of Von Weimarn (Weiser, Inorganic Colloid
Chemistry, Volume I, page 32) a red gold sol was prepared by reducing
chlorauric acid with an alkaline formaldehyde solution in order to test
the activity of alumina sols. But the change of color from red to blue
was not very sharp, therefore, an arsenious sulfide sol (Bartell "Laboratory
Manual for Colloid and Surface Chemistry") was made from arsenious oxide
and hydrogen sulfide. The stability of the As_2S_3 sol was tested with
alum. The mutual coagulation of the negative As_2S_3 sol and of a positive
Al_2O_3 sol within one hour served as a measure for the activity of the
alumina sol.

PRECIPITATION OF ALUMINA WITH AMMONIUM HYDROXIDE

In the first experiments with the ordinary centrifuge it was possible to
obtain a stable, dilute sol when 150 cc. of $\frac{n}{10}$ alum (0.015 equivalents)
were precipitated with 11 cc. of 2.8 per cent NH_4OH (slightly alkaline
reaction) and then only if, after the fourth or fifth centrifuging--the
beginning of peptization--, the suspension was vigorously stirred in the
Waring Blender. The addition of a little one per cent $AlCl_3 \cdot 6H_2O$
solution, usually 3 cc. was necessary to keep the sol stable.

The rate of adding the NH_4OH solution obviously influenced the type of
precipitate. To two solutions of the same alum concentration the same
amount of NH_4OH solution was added, to the one all at a time, but to
the other during a period of 10 minutes. In the first case a gelatinous,
bluish, more slowly settling precipitate resulted whereas the gradual
addition of NH_4OH gave a dense and white alumina which became less easily
peptized.

peptized.

In another parallel experiment different quantities of NH_4OH solution were quickly added to solutions of the same alum concentration. The larger amount of NH_4OH favored the formation of a precipitate which better settled, was earlier washed free of sulfate ions and gave a more satisfactory sol than with the use of less NH_4OH solution.

The time factor seemed to be more decisive than the amount of NH_4OH solution, for 10 cc. of 2.8 per cent NH_4OH, when quickly added, enabled a better peptization than 11 cc. of 2.8 per cent NH_4OH which were added very slowly.

When large quantities of alumina were handled in the ordinary centrifuge the precipitate could not be peptized, neither with an excess of 1 per cent $AlCl_3 \cdot 6H_2O$ solution nor with dilute HCl. Also the gradual dropwise addition of the alumina suspension to a solution of $AlCl_3 \cdot 6H_2O$--so that the peptizing agent was present in excess, at least in the beginning--did not help. Neither did the precipitation of alumina at 56° C. improve things.

Then the influences of the pH, of the concentration of the original alum solution and of the time factor were investigated in more detail. Varying quantities of distilled water were added to usually 10 grams of alum. Thus solutions containing by weight 40 per cent, 20 per cent, 10 per cent, 2 per cent, 1 per cent, 0.5 per cent and 0.25 per cent of alum were prepared. The precipitation of alumina was carried out with concentrated NH_4OH solution (28 per cent) in two sets of experiments which differed in their pH values. In one series the pH was adjusted to about 8, whereas the other series was brought to a pH around 9. Both cases showed certain characteristics. With the higher concentrations of alum milky precipitates formed, but from a concentration of 2 per cent alum the suspensions looked more and more bluish with decreasing concentration. This phenomenon was more marked at a pH of 9 than of 8. On the following day the bluish appearance changed into a greyish color. In both sets of experiments the flocs settled quickly, the sedimentation volume increased with decreasing alum concentration and the pH values decreased with the time. All suspensions were allowed to stand for some days before they were washed.

Alumina precipitates from a 10 per cent alum solution could not be peptized no matter whether they wefe run in the ordinary or in the Super Centrifuge. Alumina suspensions from 0.5 per cent and 1 per cent alum solutions, however, because nearly completely peptized after the third and fourth passage

through the Super Centrifuge, although three and four days had passed
after the precipitation. The sol from the 0.5 per cent alum solution
remained stable even without the addition of aluminum chloride. After
one week alumina precipitates from one per cent and 10 per cent alum
solutions were washed and run in the ordinary centrifuge for ten times
without getting rid of the sulfate ions and no peptization was possible.

The best result was obtained when alumina was precipitated from a 0.25
per cent alum solution with a dilute NH_4OH solution (1:6) at a pH of
9.13. As soon as the flocs had settled, the supernatant liquid was
siphoned off and replaced with distilled water. After the fifth washing
the sediment was nearly free of sulfate ions, only after several hours
a slight turbidity could be noticed in the test with $BaCl_2$. Three cc.
of 1 per cent $Al\ Cl_3 \cdot 6H_2O$ solution were added to the sediment which
occupied a much smaller volume than after the first few washings, and
the suspension was shortly boiled. Complete peptization occurred and
the sol showed a fine opalescence. It was concentrated by keeping it
at 60° C. for several hours and it remained stable. The same precipitation
was repeated, but with the difference that the settling of alumina was
brought about in the ordinary centrifuge and that the first three washings
were performed with a very dilute NH_4OH solution of a pH of 9.05. Here
the attempt of preparing a sol was unsuccessful. Also in another case,
the alumina was allowed to age for a day until the clear supernatant
liquid was decanted, then it did not get dispersed.

PRECIPITATION OF ALUMINA WITH SODIUM CARBONATE

From 0.25 per cent alum solutions alumina was precipitated with 1 $\underline{N}$ Na_2CO_3
at a pH of 9.0 and at a pH of 5.98. In neither case a stable sol could
be prepared. The suspensions looked less bluish than in the flocculation
with NH_4OH; the alumina settled down quickly so that the use of the
centrifuge was not necessary. When the precipitation took place in the
alkaline range, the alumina could be washed practically free of sulfate
ions, but not when the pH was adjusted to the acid side. In the latter
case, however, part of the alumina became peptized after the sixth washing.
But the bulk of the floc could not be broken up. Also higher alum
concentrations and the use of the ordinary centrifuge gave no satisfactory
results.

SUMMARY

The only successful attempt of preparing a stable, not too dilute alumina
sol from alum was the precipitation of alumina with NH_4OH in a very dilute

solution of alum at a pH around 9. This observation agreed with the X-ray diffraction studies of alumina gels by Weiser (Ind. Eng. Chem., November 1940, page 1487, May. 1941, page 669). He found that alumina particles precipitated from aluminum sulfate were smaller in size than those which were precipitated from the chloride or nitrate. Therefore, they had also a greater adsorption capacity for anions, which meant a decreased stability of the sol. In accord with Von Weiman's Rule Weiser observed that the primary alumina particles increased in size and correspondly showed a lessened degree of adsorption of sulfate ions as the alum concentration decreased. Another result of his studies was that the particle size of alumina increased with increasing pH.

The effect of centrifugal force was not clear. It seemed as if the ordinary centrifuge with its limited angular velocity would cause an aggregation of the primary particles into agglomerates which would resist to peptization, especially if concentrated solutions of alum were used. The high number of rotations in Sharples Super Centrifuge, however, appeared to have caused some disintegration into small particles. This factor needs further investigation.

The best sol was obtained without the use of any centrifuge and by allowing the particles to settle of their own accord. That meant a prolonged contact with the mother liquor which was full of sulfate ions. Perhaps this time was still too short to cause any considerable aging effect.

The failure of obtaining a stable sol with Na_2CO_3 was probably due to the disturbance of the carbonate ions, in addition to the trouble from the sulfate ions.

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A STUDY ABOUT THE PREPARATION OF ALUMINA SOLS FROM ALUM

In previous experiments described in Report No. 1, sodium carbonate gave a precipitate of alumina which could not be peptized to a stable sol, because the rate of its addition was slow. In this study, however, alumina sols could be prepared with sodium carbonate as precipitating agent, provided that it was added very quickly. Also sodium hydroxide could successfully be used.

In order to obtain comparable results about the effectiveness of sodium hydroxide, ammonium hydroxide and sodium carbonate, a series of experiments was carried out under the same conditions. 125 cc. of a 0.1 $\underline{N}$ solution of alum were diluted to 500 cc. in a 600 cc. beaker so that the concentration of alum was 0.0125 $\underline{N}$ or about 0.25-0.3 per cent. The precipitating agents were applied as 0.5 $\underline{N}$ solutions and added to the well-stirred solution of alum as quickly as possible. After the measurement of the pH the suspensions were allowed to settle. The supernatant liquids were decanted, fresh water was added and the alumina flocs again settled. The washings were repeated. Mostly after the sixth time, part of the alumina became peptized. Then the sediment was centrifuged to concentrate the alumina and 0.6 cc. of a one per cent solution of $AlCl_3 \cdot 6H_2O$ (6 mgm. or 7.5×10^{-2} milliequivalents) were added to it. Finally the suspensions were heated, which was always necessary to bring about a good peptization.

Precipitation with 0.5 N NaOH

The precipitations covered a pH range from 4.5 to 10.0. In the acid range no peptizable precipitate could be obtained. The best sols resulted when alumina formed at a very high pH. But from a pH around 8.5, part of the alumina already dissolved to aluminate in the excess of base so that this method is not economical. Furthermore most sols did not remain stable for a long time; after a few days they became very viscous and finally set to a gel.

Precipitation with 0.5 N NH$_4$OH

Here the pH range extended from 6.05 to 9.0. Also, here all attempts to prepare a stable sol by precipitating alumina on the acid side failed. Fairly good sols were prepared already from a pH of about 7.5, but only from 8.0 the sols looked nearly clear and showed a fine bluish appearance and a sharp Tyndall cone when illuminated with a strong light. The adjustment to a higher pH value, from about 8.5, required very large amounts of NH_4OH, which can also be seen from the pH-concentration curves of Weiser (Ind. Eng. Chem., November 1940, page 1487) . At this alkalinity, the solubility of alumina

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was no more negligible. Another observation showed that, with increasing pH
the alumina floc settled quicker and that its sedimentation volume became
smaller.

Precipitation with 0.5 Na_2CO_3

Precipitations were carried out in a pH range from 7.05 to 8.40. The acid
side of the pH scale was no more investigated, after some experiments with
1 $\underline{N}$ Na_2CO_3 down to a pH of 4.55 had already been without success. The alumina
which had formed at a low pH still contained considerable quantities of sulfate
ions after several washings; nevertheless it started to become peptized,
sometimes already at the fourth or fifth washing. In systems of originally
high pH values, the alumina was never completely washed free of these disturbing
ions, but their concentration was reduced to a minimum so that their presence
could be detected only in a rather large quantity of the sediment and even
then it took some time until a precipitate of $BaSO_4$ appeared in the test. From
a pH of 7.5 upwards, good sols were obtained, but always the peptization
proceeded slowly and required boiling of the suspension. The observations
with Na_2CO_3 fit into the results of Weiser's x-ray investigations of alumina.
He found that alum and sodium carbonate formed the most highly dispersed
crystals of $\gamma\text{-}Al_2O_3 \cdot H_2O$ at a pH between 5.5 and 6.5 and that the particle
size of alumina increased with increasing pH. Corresponding to this effect
the adsorption capacity of alumina for sulfate ions should decrease, which
actually was observed.

Comparison of the Effects of 0.5 $\underline{N}$ NaOH, 0.5 $\underline{N}$ NH_4OH and 0.5 $\underline{N}$ Na_2CO_3 at a pH of 8

Finally alumina was precipitated at the same time with 0.5 $\underline{N}$ NaOH, 0.5 $\underline{N}$ NH_4OH
and 0.5 $\underline{N}$ Na_2CO_3 at a pH of about 8 and under the same usual conditions.
NH_4OH caused a more bluish appearance of the suspension than NaOH, and this
more than Na_2CO_3. The rates of settling decreased in the order NaOH, NH_4OH,
Na_2CO_3, whereas the sedimentation volumes showed the reverse order. These
observations may again be correlated to Weiser's studies according to which
at a given pH the size of the primary alumina crystals fell off from NaOH to
NH_4OH and then to Na_2CO_3. As expected, the larger NaOH particles settled
quicker. Their close packing to a smaller sedimentation volume was probably
related to the degree of hydration. The alumina flocs from NH_4OH and Na_2CO_3
were easily and completely peptized, but not those from NaOH. The test for
sulfate ions always was positive, but their concentration apparently fell
below a critical value in case of NH_4OH and NaOH.

The decisive factor in the successful preparation of an alumina sol seems to
be the very first step of the whole process, the method of precipitation. This
conclusion was drawn when alumina was once more precipitated with 0.5 $\underline{N}$ NH_4OH
at a pH of 8. The suspension was split into two parts. One of them was
allowed to age for 1 3/4 hours before it was washed, whereas in the other

part the alumina was repeatedly separated from the wash water not by mere settling, but in the centrifuge. In both cases alumina could be peptized to a good sol. But the time factor and , to a less extent, the centrifugal force affected the stability and thus proved to be of influence. After some time the sols set to a gel.

With tap water and softened water, it was quite impossible to peptize the alumina which showed a strong yellow color due to the presence of colloidal substances. The sulfate ion concentration in the water was too high to allow peptization.

It is difficult to decide which of the two reagents, NH_4OH and NaOH, should be preferred in practice. Although the use of Na_2CO_3 required a much larger amount, as it is also evident from the x-ray concentration curves of Weiser, its cost, taken on a weight basis, is much smaller than that of NH_4OH.

All the sols which were prepared contained alumina in a concentration of only 0.5-0.8 per cent. In order to obtain sols with a higher alumina content larger quantities of the reagents were used, e.g. 20 grams of alum in 3600 cc. water were precipitated with 400 cc. of 0.5 $\underline{N}$ NH_4OH at a pH around 8. Here the original alum concentration amounted to about 0.5 per cent and was already too high to allow the alumina floc to settle quickly. The rate of settling could be increased when the suspension was split into two parts and washed in two 4-liter beakers. But it did not help in obtaining a good sol. Peptization was either impossible or, at best, incomplete so that a turbid sol resulted. If alum was added to NH_4OH, the alumina consisted of small particles which could not be peptized.

Precipitation with 0.1 $\underline{N}$ $Ba(OH)_2$

Whereas in the precipitations with NaOH, NH_4OH, and Na_2CO_3 the sulfate ions can only gradually and incompletely be removed from the system, the use of $Ba(OH)_2$ with the resulting formation of $BaSO_4$ and Al_2O_3 should immediately eliminate the harmful influence of these ions. Then it should be possible to peptize the alumina floc by adding $AlCl_3 \cdot 6H_2O$ and to separate the sol from the insoluble $BaSO_4$ by filtration. 100 cc. of 0.1 $\underline{N}$ $Ba(OH)_2$ were diluted to 400 cc. and were slowly precipitated with 0.1 $\underline{N}$ alum in a slightly alkaline medium. Thus during the whole process no excessive sulfate ions were present. A better settling floc formed when the precipitation was done at 60° C. Then adsorbed sulfate ions were more readily washed off from the precipitate than in case of the precipitation at room temperature. 1 cc. of one per cent $AlCl_3 \cdot 6H_2O$ solution was added and the suspension was heated to 70-80° C. for about one hour, and filtered afterwards. Sometimes a very dilute sol of alumina

was obtained. It showed a Tyndall cone and $K_4[Fe(CN)_6]$ produced a floc which was soluble in HCl. The low yield of alumina sol may be explained on the assumption that the negatively charged $BaSO_4$ particles and the positively charged alumina micelles mutually precipitated each other and formed irreversible aggregates. It seems to be worthwhile continuing these studies about the optimum conditions, for the use of $Ba(OH)_2$ would make the preparation of alumina sols relatively simple and the valuable by-product $BaSO_4$ would be obtained.

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A STUDY ABOUT THE PREPARATION OF ALUMINA SOLS FROM ALUM

Precipitation of alumina by the interaction of alum and barium compounds.

The experiments with alum and barium hydroxide which were mentioned at the end of Report No. 2 were continued. If the precipitation was carried out at room temperature and if aluminum chloride, the peptizing agent, was added immediately after the formation of the alumina and barium sulfate precipitates, a stable alumina sol could be obtained at a pH around 4.5 and on heating the suspension to 60-70° C. for some hours. Unfortunately the sols were very dilute and a large part of the alumina was still in the precipitated form.

In a modified procedure barium hydroxide was replaced by a saturated solution of barium aluminate. Alum was added to it until a pH of about 7 was reached. Then immediately aluminum chloride was added so that the pH of the suspension dropped to around 4.5. Here the effect of the rate of addition of alum was very striking. If the precipitation was carried out slowly, large flocs formed, settled quickly and left the supernatant liquid only slightly turbid, whereas the quick addition of alum resulted in a fine bluish turbidity of the supernatant liquid, which meant the formation of a sol. It was not quite free of finely dispersed barium sulfate and again not very concentrated. Precipitation at higher temperatures caused the formation of larger particles which settled easily, but they could not be peptized.

It seems to be very difficult to prepare alumina sols with a satisfactory quantitative yield by the use of alum and barium compounds, although, at first sight, the idea to eliminate the harmful sulfate ions by the formation of the insoluble barium sulfate appears very attractive and inviting. But barium sulfate itself introduces new complications. It itself is present in the colloidal state, as a negatively changed sol of high surface reactivity and thus tends to flocculate the positively charged alumina micelles. At boiling temperature a coarser floc of barium sulfate was obtained, but at the same time alumina became rather insoluble.

Precipitation with sodium hydroxide

The application of a different technique succeeded in the preparation of alumina sols with NaOH as precipitating agent. Both reagents were added simultaneously to water so that the solution was always dilute.

This should reduce the influence of the quantities to be used. The details of the procedure were as follows: To 300 cc. of distilled water in a 400 cc. beaker, 50 cc of roughly $\frac{n}{1}$NaOH and 50.6 cc. of approximately $\frac{n}{5}$Al$_2$(SO$_4$)$_3 \cdot$18H$_2$O were simultaneously added within three to four minutes. NaOH was added at a higher rate than alum to keep the system always alkaline, at a pH between 8 and 9 during most of the time. The final pH was 7.6. The alumina flocs showed a bluish white appearance and, in the beginning, settled slowly. It did not make any difference if the suspension was allowed to stand for a day and then was centrifuged several times or if it was worked up immediately. Nor did it have any influence if the alumina was washed by allowing it to settle and then by decanting the supernatant liquid or by the use of the centrifuge. In any case, a stable sol resulted when 5 cc. of a one per cent AlCl$_3 \cdot$6H$_2$O solution were added and when the suspension was boiled. Even smaller quantities than 5 cc. were sufficient to cause peptization, but an excess of AlCl$_3 \cdot$6H$_2$O was purposely used. The sols looked bluish and yellowish when viewed in transmitted light, but somewhat turbid. They did not clear up on the addition of some more aluminum chloride. The concentration of these sols varied between 1.1 and 1.3 per cent of Al$_2$O$_3$.

## Precipitation with sodium carbonate

Also here the above described modified technique gave good results. In order to use again approximately equal volumes of both reagents, sodium carbonate had to be applied as a 1$\underline{N}$ solution. The other details of the procedure were as before with the exception of different adjustments of the final pH value. An excellent peptization was achieved when the precipitation was carried out to a pH value of 7.2. A sol of a fine bluish color resulted which looked almost like a clear solution but exhibited a sharp Tyndall cone when it was illuminated with a strong light source. The precipitation could be extended even into the acidic range of the pH scale. Alumina flocs which formed at a pH of 6.5 could easily be peptized to a very stable sol which appeared only slightly more turbid than that obtained from a precipitate at a pH of 7.2. With a pH of 6, however, the sol became very viscous and often turned into a gel. Whereas with NaOH as precipitating agent it did not matter whether the alumina floc was separated from the liquid by mere settling or by the use of the centrifuge, with Na$_2$CO$_3$ more viscous sols or even gels formed when washing was accomplished with the centrifuge. This behavior was checked several times and always confirmed. The time factor was not important; good sols were obtained as well when the suspension was washed immediately as when it was allowed to stand overnight.

In the first two or three washings, each with about 700 cc. of H$_2$O in a 1 liter beaker, the alumina floc settled slowly and the supernatant liquid contained small particles. After the third washing large flocs of a bluish appearance formed and settled quickly so that the supernatant liquid was clear. Usually after the sixth washing a slight peptization

started. Then the alumina was concentrated by centrifuging it in the ordinary centrifuge. 5cc. of a one per cent $AlCl_2 \cdot 6H_2O$ solution made the system sufficiently acid and peptization occurred on boiling.

The same results were obtained when alum was quickly added to a dilute solution of sodium carbonate. In both techniques the system was kept alkaline during the precipitation. In such a medium the alumina micelles were probably negatively charged so that they should not so much be affected by the sulfate ions as if they were positive micelles.

The x-ray studies of alumina by Weiser have shown that, at a given pH with different precipitants the size of the primary crystals (γ-$Al_2O_3 \cdot H_2O$) falls off in the order NaOH, NH_4OH, Na_2CO_3. Correspondingly the same order was observed for the rate of settling and the inverse order for the sedimentation volumes. A smaller particle size means a higher adsorption capacity. Therefore one would expect that alumina precipitated with Na_2CO_3 should adsorb more sulfate ions and therefore should be less suited for peptization than when formed with NaOH. But just the opposite happened. An explanation for this surprising observation may be found in the assumption that the carbonate ions very effectively compete with the sulfate ions for being adsorbed on the surface of the alumina micelles. At least a large part of the sulfate ions may be excluded from the available spots of adsorption by such a "protective barrier" of carbonate ions. In agreement with such an assumption was the test for sulfate ions in the washed sediment. A slight turbidity of $BaSO_4$ was visible only after some time, sometimes not until the following day. Heating would displace the equilibria.

$$2H^+ + CO_3^{--} \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons H_2CO_3 \rightleftharpoons H_2O + CO_2\uparrow$$
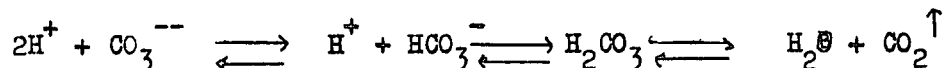
to the right side and actually a strong gas evolution preceded the peptization to a sol.

Also the sols prepared with Na_2CO_3 contained about 1.1 to 1.3 per cent Al_2O_3. They proved to be more stable than those made with NaOH or NH_4OH. Even after nearly three months some of them did not show any apparent change.

Thus a method seems to be found to prepare stable alumina sols from alum and sodium carbonate at a pH around the neutral point. With sodium hydroxide and ammonium hydroxide which are both more expensive good sols were obtained only when the precipitation was made in the alkaline range. There the solubility of alumina is no more negligible so that part of it, although a small one, is lost. But also with Na_2CO_3 the difficulty of preparing higher concentrated sols has still to be overcome. The ordinary centrifuge does not permit a concentration higher than 1 to 1.5 per cent

Al_2O_3. When the Sharples supercentrifuge was used, alumina could not be peptized, no matter which was the precipitant. But the systems with Na_2CO_3 did not appear to be hopeless. They were nearly free of sulfate ions and on boiling a lumpy gel formed like that of silicic acid when HCl is added to water glass. It looked nearly transparent. It may be that a larger quantity of the peptizing agent and a very cautious heating and stirring will make the preparation of a concentrated sol possible. Further experiments in this direction could no more be undertaken because of the necessity of overhauling the supercentrifuge, but, as soon as this apparatus is again available, they will be continued.

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