STUDIES ON SOME REACTIONS OF PORTLAND CEMENT

by

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This thesis presents a summary of the research conducted during the year June 1950 - June 1951 under a research fellowship established at Union College by the North American Cement Corporation in 1948. The research was performed in the Butterfield Laboratory at Union College under the direction of Professor Charles B. Hurd of Union College. The North American Cement Corporation was represented in conferences by Mr. John J. Porter and Mr. H. F. Kichline, To both of whom we are very much indebted for many helpful suggestions and ideas.

THESIS

STUDIES ON SOME REACTIONS OF PORTLAND CEMENT

Abstract: Studies are made on 1. the mechanism of cement setting, 2. cement - sawdust mixtures, 3. the effect of soluble compounds on cement, 4. cement - latex mixtures and 5. cement - plastic compositions.

General Introduction:(1,2) Strictly speaking, the term "cement" is a general term for any substance which causes two bodies to adhere together. The binding together of stones with a cement to form a solid structure has been used since the beginning of recorded history. The pyramids of Egypt employing a cement between the stone blocks exhibit the antiquity of such construction. No one knows when the use of cementing material was discovered but it was probably soon after the intelligent use of fire.

Portland cement, a type of cement (not a brand name), is a comparative newcomer to the long list of cementing materials. This cement dates back to about 1825 and it has been used extensively only in this century. Portland cement is made by heating limestone with clay or and equivalent composition to about 1450°C at which temperature certain reactions take place giving a product known as "clinker". The clinker is ground with 2 - 3 percent of gypsum, which is added to retard setting, to give portland cement. The principal compounds in portland cement are the substances Ca_2SiO_4, Ca_3SiO_5, and $Ca_3(AlO_3)2$. Portland cement is a hydraulic cement i.e. it will form under water. The setting of the cement is related to the hydration of these compounds, the hydration of tricalcium silicate being of special importance.

The composition of portland cement is given in the following table.(2)

Composition of Portland Cement

Oxide	CaO	SiO_2	Al_2O_3	Fe_2O_5	MgO	SO_3	Na_2O, K_2O
Percent	58-67	19-26	4-11	2-5	0-5	0-2.5	0-3

The opportunities for research on portland cement are many. Even without elaborate or special equipment, many research topics on portland cement may be satisfactorily conducted in a college laboratory. The topics of research conducted at Union College on portland cement include:

1. An attempt to find information concerning the chemical processes occuring during the setting of portland cement.
2. Correlating the information with some theory of set mechanism.
3. An investigation of possible new uses for portland cement.
    a. Portland cement with siliceous aggregate as a structural material.
    b. Portland cement with other inert aggregate as structural material with specific properties.
    c. Portland cement with electrolytic and non-electrolytic additions for varied properties such as variations in time of setting, heat of setting, strength, density, color, etc.
    d. Portland cement as a reagent chemical. Non structural chemical uses.

It was decided to concentrate the work of 1950 - 1951 year on point three, new and extended uses for portland cement. Five separate investigations were undertaken and the five following sections describe the work covered.

These are:

SECTION I. – The mechanism of setting of portland cement.

SECTION II. – Portland cement-sawdust mixtures.

SECTION III. – The effect of soluble compounds on portland cement.

SECTION IV. – Mixtures of portland cement and latex

SECTION V. – Cement – plastic compositions.

REFERENCES

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pp 309 - 310

SECTION I

The Mechanism of Setting of Portland Cement Pastes

As foundation work for the general program of cement research sponsored by the North American Cement Corporation, the literature search on the mechanism of setting of portland cement was continued. A detailed search in Chemical Abstracts for the period 1930 - 1950 was made and 458 pertinent references were collected and classified. Although the problem of the mechanism of set was not directly investigated in the year 1950 - 1951, it is hoped that these references will be of use in subsequent investigations.

SECTION II

Portland cement-sawdust mixtures.

Abstract: One hundred thirty blocks of cement-sawdust compositions were prepared and the effect of various pretreatments of the sawdust, admixtures to the material, and curing conditions were studied and compared as to their effect on the transverse strength and hardness of the set and cured product.

Introduction and Historical:(1,2) Since industry is constantly looking for new and better building materials, it is quite reasonable that portland cement-sawdust mixtures should be investigated. The theoretical objective of such an investigation would be to produce a material which would combine to advantage the properties of wood and cement i.e. cheapness, lightness, ease of working, tensile strength, low thermal conductivity, ability to take and hold nails, and resistance to vibration and impact. The source of raw materials for such a product would be almost limitless, since cement is produced on a large scale and since sawdust is readily available in tremendous quantities.

The use of sawdust with various binders is not a new idea. Ground wood was used in pottery in ancient Arabia. The practice of adding sawdust to plaster for use in walls, roofs, etc. has been used for some time by the Europeans. The addition of sawdust to mortar for stuccoing frounts of houses has found acceptance in America.

The use of sawdust as an aggregate for portland cement dates back at least to the beginning of this century. During the last war cement-sawdust mixtures were used for fabricating walls of huts, floor finishes, lining roofs and other minor uses.

Theoretical: Portland cement-sawdust mixtures are, as the name implies, fundamentally composed of mixtures of portland cement and sawdust. However, products made simply by combining portland cement, sawdust, and sufficient amount of water for reaction are in general not satisfactory, being weak, non-uniform, and hard to manage. These adverse properties have been attributed to a number of causes. Tannic acid is known to be detrimental to cement. Thus tannins and tannic acid in wood might be expected to be a harmful factor. Sugars are known to have adverse effects on the setting of cement and likewise other soluble carbohydrates in cement might also be injurious. It is possible that wood may exhibit a buffering action on the early stages of alkali formation and alter the setting action of the cement when water is first added. In certain instances aromatic oils present in timber might affect the hydration of the cement.

Two general treatments have been devised to minimize the above mentioned effects and produce a sounder product. These are (1) pretreatment of the sawdust and (2) admixture to the cement-sawdust mixtures.

Processes involving pretreatment of the sawdust can be separated into several categories. These have been outlined by Parker(3) as follows:

(1) Treatment involving partial oxidation of the wood (including partial charring).

(2) Treatment designed to waterproof the sawdust and thus prevent solvent action.

(3) Treatment designed to neutralize with alkali, to precipitate tannates or to treat with sulfates.

According to Parker this latter treatment (item 3) has been the most successful and this treatment was used as a basis for further study. Parker suggests the following procedure for pretreatment of the sawdust as under item 3 above:

Boiling the sawdust in water

Draining and washing with water

Reboiling with a solution of ferrous sulfate in water.

Draining and rewashing.

SECTION II

Boiling the sawdust with water serves to extract some soluble materials e.g. some soluble carbohydrates and to perhaps remove some oils by steam distillation. The addition of ferrous sulfate serves to precipitate tannins as ferric tannate (on oxidation).

Processis involving admixture to the cement generally consist of accelerating the setting of cement so that the mechanism of setting may get under way before the harmful effects of dissolved substances etc. from the wood have opportunity to act.

Experimental: The study of sawdust-cement mixtures was based on observations of the products formed by the two treatments outlined above, namely (1) pretreatment of the sawdust and (2) admixture to the cement-sawdust mixture. The effect of variations in curing conditions was also studied.

The general procedure used in preparing samples was to mix the dry sawdust (pretreated or raw) with the dry cement and admixture (if dry). This was done in a 600 ml. beaker, stirring being done by hand with a small round file as a stirring rod since glass rods proved too apt to break. When the dry material had been mixed, water from an automatic buret plus any other liquid additions were added. The mixture was thoroughly stirred for one or two minutes and was then poured into a standard mold forming a briquette 6X1X1". The mixture was allowed to set until firm. The briquette was then removed from the mold, stored for curing, and sent to the Catskill laboratories of the North American Cement Corporation for testing.

The method of preparation of the briquettes should be noted. Serveral unsuccessful attempts were made in forming briquettes because of the tendency of the set briquette to stick to the material (glass) used as the base of the mold. This difficulty was solved by using the following procedure. A piece of wet cellophane was stretched smoothly over a piece of glass plate approximately 10" by 4". The mold, which was open on the top and bottom, was well greased with vaseline on all portions coming in contact with the cement and was placed on the cellophane in the center of the plate. The cellophane on drying shrunk slightly, forming a hard, very smooth base for the mold. For especially tenacious samples the cellophane also was greased. When the sample had become firm the mold was removed and the briquette, still on the cellophane and plate was allowed to set thoroughly before it was removed. The necessity of removing the mold from the unset sample, due to the small number of molds available, made this special procedure necessary since a small amount of sample sticking to the mold on removal would ruin the briquette for shear tests. This procedure was about ninety percent successful.

The method of boiling and washing the sawdust was as follows. The sawdust was placed with an excess of water in a five liter round bottom flask which was placed off center over a gas burner so that heat was not evenly distributed over the bottom of the flask. This uneven heating caused convection currents to rapidly spin the sawdust in the flask, thereby preventing the sawdust from burning, allowing much more sawdust to be treated at once, and assuring equal treatment for all portions of the material. After a given time the mixture of sawdust and water was removed from the heat and was poured into a large cloth bag suspended in a sink below two faucets. The faucets were then turned on full force, churning up the sawdust in the bag and thoroughly washing the material. Washing could be continued in this manner for long periods with little attention.

The following methods of treatment of the sawdust before mixing with cement were employed:

1. The sawdust was used raw i.e. as it came from the lumberyard. Raw sawdust was not compatible with cement in simple cement- sawdust water pastes. The freshly made material was uneven in texture and hard to handle. Consider-

able patience was required to properly fill a mold with this material. After washing, 0.58% of raw sawdust remained.

2. The sawdust was boiled in water for one hour, washed and dried. The hot water drained from the sawdust was colored a light brown and on evaporation left a gummy material. On boiling, the steam from the flask had a fragrant odor indicating that some oils etc. were probably being steam distilled into the atmosphere. The purpose of this procedure as mentioned before was to dissolve soluble carbonates, etc. and remove some volatile material.

3. The sawdust was extracted with acetone. The material was placed in a Soxhlet extractor which was operated for one hour at which time no more colored material was being extracted from the sawdust. The acetone became yellowish brown after a few minutes of operation. A quantitative determination in which weighed raw sawdust was extracted with acetone for one hour removing all soluble colored material, then was extracted for another hour with fresh acetone (no change visible), dried and reweighed, indicated that 2.8% by weight of dry raw sawdust was extracted. The purpose of extracting the sawdust with acetone was to remove organic products not soluble in water but soluble in an organic solvent.

4. The sawdust was boiled in water one hour and washed as in (2), then boiled in an electrolyte solution (abour 200 g. electrolyte per liter) for one hour, thoroughly washed again and dried. The purpose of this procedure was to react some of the adverse materials chemically and render them harmless. This process was intended principally to eliminate the deleterious effects of the tannates. The following electrolytes were used:

a. Ferrous sulfate - the sawdust after treatment retained a brown color.

b. Manganous chloride - the sawdust after treatment retained a faint brown tinge.

c. Cupric sulfate - the sawdust after treatment retained a light brown color.

d. Lead acetate - the sawdust after treatment retained an orange color. A cloudiness was noticed when the solution of lead acetate was made up using tapwater. This was probably due to precipitation of carbonate. This precipitate probably remained in the treated sawdust.

e. Potassium dichromate - the sawdust after treatment retained a dark brown color, possibly from partial oxidation.

f. Sodium silicate - the sawdust after treatment retained an orange color. After ashing 1.8% by weight of the dry treated sawdust remained. (see 1)

g. Sodium hydroxide - the sawdust after treatment retained an orange color. After ashing 2.0% by weight of the dried treated sawdust remained. (see 1)

h. Ferric chloride - the sawdust after treatment retained a dark brown color. After ashing 1.8% by weight of the dried treated sawdust remained. (see 1) The ash was voluminous and bright.

Admixtures to the cement - sawdust mixtures were varied but special attention was paid to admixtures which accelerated the set of cement. Among the admixtures employed were powered anhydrous $CaCl_2$, Cr_2O_3, NH_4CNS, CaO, $AlCl_3$, Na_2SO_3, Na_2SO_4, $K_4Fe(CN)_6$, and powered sulfur. Of particular notice was an aqueous solution of five chlorides mentioned by Brocard,(4) consisting of $CaCl_2$ 18.2, $AlCl_3$ 5.5, $FeCl_3$ 0.15, $BaCl_2$ 0.2, $NaCl$ 1.0 g., and water to make 100 ml. This solution and other accelerators to a lesser degree when added caused a remarkable change in the physical nature of the sawdust - cement paste. The paste became homogeneous in appearance, lighter in color, and weight, and many times easier to handle and mold.

SECTION II

TABLE I

Cement: Catskill regular portland cement

Sawdust: Series "XA" and "XB" - principally pine sawdust

Series "XC" - a mixture of pine and oak sawdust passed through a no. 10 sieve to remove coarse chunks of wood.

The mixtures are given in terms of volume ration of constituents, one part by volume equaling 15.5 ml.

The following tabulation gives the composition and various data for the 130 samples prepared for testing. The tests on the transverse strength and hardness were made by the North American Cement Corporation laboratories at Catskill, N.Y.

Sample	Cem.	Saw.	Water.	Treat. of Sawdust	Acc.	Type of Accel.	Transv. (1) Strength	(2) Hardness
XA 1	10	10	5.8	raw			130	3640
2	8	8	4.1	"			130	3960
4	5	10	4.7	"			60	1080
5	3	9	3.4	"			10	140
7	8	8	4.1	"			125	4120
8	5	10	4.1	"	.5	mixed chl .	130	2380
11	8	8	4.3	acetone			140	5940
12	8	8	3.9	"			120	6020
13	5	10	3.7	"			75	2540
17	8	8		"	.67	mixed chl.	140	8760
18	5	10	4.5	"	.67	" "	90	2400
19	5	10	4.6	raw	1.0	solid $CaCl_2$	90	1760
20	5	10	3.5	"	1.0	mixed chl.	100	2220
21	5	10	3.8	"	1.0	" "	60	1440
23	4	12	4.7	acetone	.67	" "	80	1580
24	5	10	3.9	Fe SO_4 sol.			80	2120
25	5	10		$MnCl_2$ sol.			60	1720
26	4	12	6.1	acetone			30	720
27	4	12	5.9	$MnCl_2$ sol.			40	520
28	4	12	4.7	raw	1.0	mixed chl.	60	740
30	4	12	4.5	$MnCl_2$ sol.	1.0	" "	60	1380
31	5	10	3.5	" "	1.0	" "	100	2580
32	5	10	3.7	raw	3.0	$CaCl_2$ dry	80	2860
33	5	10	3.7	"	2.0	" "	90	2900
34	5	10	4.5	"	1.0	" "	100	2500
XB 1	5	10	4.1	"	.5	solid $CaCl_2$	150	4520
2	5	10	4.7	"	.25	" "	110	2420
3	5	10	4.6	$CuSO_4$			80	1540
4	8	8	3.7	"			160	5420
6	4	12	4.6	"			50	1000
7	5	10	4.5	$PbAc_2$			80	1580
8	4	12	4.9	"			50	920
9	5	10	4.4	acetone	.03	Cr_2O_3	80	1640
10	5	10	4.0	$PbAc_2$	1.0	mixed chl.	120	2280
12	4	8	4.1	Acetone	4.0	wood flour mixed chl.	80	1760
13	5	10	3.2	$PbAc_2$	1.0	mixed chl.	110	2860
14	5	10	3.2	$K_2Cr_2O_7$			100	2620
16	5	10	3.8	"			80	1580
17	4	12	3.7	"			60	1120
18	5	10	2.2	"	1.0	mixed chl.	150	4080
19	4	12	3.2	"	1.0	" "	100	1800
20	5	10	3.2	$FeSO_4$			100	2300
21	5	10	2.4	"	1.0	" "	160	4960
22	4	12	4.2	"			60	1020

(1) Pounds required for failure across a 3" span.

(2) Total load on a 1" X 2" surface.

Sample	Cem.	Saw.	Water	Treat. of Sawdust	ACC.	Type of Accel.	Transv. Strength	Hardness
XB 24	5	10	4.4	acetone	.33	NH_4CNS	100	2460
25	5	10	3.9	"	1.0 .33	mixed chl. NH_4CNS	120	2920
26	5	10	2.6	$K_2Cr_2O_7$	1.0 .33	mixed chl. NH_4CNS	180	4260
27	5	10	3.2	"	1.0 .33	mixed chl. NH_4CNS	140	3100
28	5	10	4.5	acetone	1.0	solid CaO	80	1580
29	5	10	4.8	$PbAc_2$	1.0	solid CaO	90	1800
30	5	10	4.1	$K_2Cr_2O_7$	1.0	solid CaO	100	2100
31	5	10	4.3	$FeSO_4$	1.0	solid CaO	80	1560
32	4	12	2.8	$K_2Cr_2O_7$	2.0	2N $CaCl_2$	110	1960
33	4	12	4.5	$CuSO_4$	.33	$AlCl_3$	50	840
36	5	10	3.2	$K_2Cr_2O_7$	.33	Na_2SO_3	130	3540
37	5	10	?	"	.33	$K_4Fe(CN)_6$	110	2500

Sawdust used in XC series is mixed, pine with oak.

Sample	Cem.	Saw.	Water	Treat. of Sawdust	ACC.	Type of Accel.	Transv. Strength	Hardness
XC 1	8	8	4.0	raw			160	5260
2	8	8	3.9	"			160	5200
5	5	10	4.2	"			20	100*
6	5	10	3.6	"			20	500*
7	5	10	2.7	"	1.0	mixed chl.	80	2180
9	8	8	3.7	acetone			140	5360
10	8	8	3.6	"			140	4680
11	5	10	2.7	"			90	1500
12	5	10	4.2	"			70	1200
13	5	10	4.3	"			120	2500
15	4	12	3.8	"			100	2080
16	8	8	4.5	water glass			160	4680
17	8	8	4.2	" "			160	5600
18	5	10	4.2	" "			130	2060
19	5	10	4.4	" "			110	1880
20	5	10	4.1	acetone			100	1700
21	5	10	4.1	"			130	2160**
22	5	10	4.1	"			90	1400
23	5	10	3.9	"			130	2500**
25	5	10	3.2	water glass	1.0	mixed chl.	180	4060

*Block app. defective.
**Cured 2weeks, damp chamber.

Sample	Cem.	Saw.	Water	Treat. of Sawdust	Acc.	Type of Accel.	Transv. Strength	Hardness
XO 26	5	10	3.2	water glass	1.0	mixed chl.	180	4300
27	4	12	4.1	" "		" "	90	1800
28	4	12	3.7	" "	1.0	" chl.	240	2540
29	8	8	4.0	NaOH			230	6700
30	8	8	3.9	"			170	6640
31	5	10	4.3	"			150	2320
32	5	10	4.8	"			130	1640
33	8	8	3.1	"	1.0	mixed chl.	220	9750
34	5	10	3.5	"	1.0	" "	160	3720
35	8	8	2.7	"	1.0	" "	230	8900
36	5	10	3.0	"	1.0	" "	180	3900
37	5	10	4.3	acetone			120	2100
38	5	10	4.1	"			100	1700
39	5	10	3.5	"	1.0	mixed chl.	130	3100
41	6	12	4.6	W.G.			130	2120
42	8	8	3.8	$FeCl_3$ sol.			-	-
43	8	8	3.5	" "			90	2080
44	8	8	2.7	" "	1.0	mixed chl.	170	6260
49	8	8	3.9	" "			70	1020
51	5	10	2.9	" "	1.0	mixed chl.	120	2520
52	5	10	4.5	acetone			90	1620
53	5	10	4.0	"	.5	solid Na_2SO_4 10 H_2O	80	1260
54	5	10	3.9	"	.5	ditto	100	1500
55	5	10	3.9	"	1.0	ditto	80	1400
56	8	8	3.2	$K_2Cr_2O_7$sol.			220	6860
57	8	8	3.2	" "			180	7380
58	8	8	2.3	" "	1.0	mixed chl.	200	9020
59	8	8	2.3	" "	1.0	" "	190	8540
60	5	10	3.2	" "			170	3740
61	6	12	3.9	" "			130	3360
62	6	12	2.8	" "	1.2	" "	230	5900
63	6	12	2.7	" "	1.2	" "	210	6240
64	4	12	3.8	" "			100	1580
65	4	12	3.5	" "			130	1920
66	4	12	2.6	" "	1.0	mixed chl.	160	3700
67	4	12	2.6	acetone	1.0	" "	170	3760
68	5	10	4.5	"	1.0	sulfur	110	2100
69	5	10	4.3	"	2.0	"	130	2320
70	5	10	4.2	"	3.0	"	90	2000
71	5	10	4.8	"	4.0	"	90	1680
72	5	10	4.3	"	.67	"	100	1920
74	5	10	3.6	"	.16	"	150	2360
75	5	10	2.9	"	1.0 1.0	sulfur mixed chl.	190	5040

SECTION II

TABLE II

Sample	Cement	Sawdust	Treatment of sawdust	Trans. St.	Hardness
XC 1	8	8	raw	100	5260
XC 10	8	8	acetone	140	4680
XC 17	8	8	Na_2SiO_3	160	5600
XC 29	8	8	NaOH	230	6700
XC 43	8	8	$FeCl_3$	90	2080
XC 56	8	8	$K_2Cr_2O_7$	220	6860
XC 76	8	8	boiled water	220	7560
XC 6	5	10	raw	20	500
XC 11	5	10	acetone	90	1500
XC 18	5	10	Na_2SiO_3	130	2080
XC 31	5	10	NaOH	150	2320
XC 60	5	10	$K_2Cr_2O_7$	170	3740
XC 78	5	10	boiling water	140	2960
XC 64	4	12	$K_2Cr_2O_7$	100	1580
XC 83	4	12	boiling water	90	1400

Table II gives certain data taken from table I rearranged to show the comparative effectiveness of various pretreatments of sawdust without admixture of electrolytes to the samples. It is interesting to note that one of the most effective methods of pretreatment is also the simplest and cheapest: merely boiling the sawdust with water and washing. The significance of this treatment was not realized until late in the project and few samples were made. Treatment with potassium dichromate is the most beneficial of the electrolyte treatments, being perhaps slightly more effective than treatment with boiled water. Partial oxidation of the sawdust by the dichromate might be a contributing factor to strength. It was noted that the sawdust after dichromate treatment was very dark in color. Treatment with ferric chloride was unique in that the product prepared exhibited less strength than samples made with the raw sawdust. Acetone extraction proved to be of little value. With the exception of ferric chloride, treatment with electrolytes produced a stronger product than was obtained with raw sawdust but in general the product was less strong than that obtained with sawdust boiled with water only. Since boiling with water preceeded treatment with electrolytes, the effect of the electrolytes (excluding potassium dichromate) is not advantageous to the strength of the product.

TABLE III

(Sawdust extracted with acetone)

Sample	Cement	Sawdust	Admixt.	Transverse strength	Hardness
XB 9	5	10	0.03 Cr_2O_3	80	1640
XB 12	4	8	4.0 wood flour	80	1760
XB 24	5	10	0.33 NH_4CNS	100	2460
XC 11	5	10		90	1500
XC 13	5	10	1.0 mixed chloride	120	2500
XC 28	5	10	1.0 pwd. CaO	80	1580
XC 55	5	10	1.0 $Na_2SO_4 \cdot 10H_2O$	80	1400
XC 68	5	10	1.0 pwd. S	110	2100

Table III lists some data taken from table I comparing the effect of several admixtures on acetone treated sawdust. By far the most effective admixture for producing strength was Brocard's five chloride mixture. Accelerators are most effective in increasing strength. Certain other substances are beneficial such as sulfur.

Damp curing the two blocks (XC 21, 23) had a considerable effect in increasing the strength of the samples.

Summary: As a result of test on the transverse strength and hardness of 130 samples of cement - sawdust mixtures, the following may be concluded:

1. Incorporation of sawdust with cement decreases the density of the product and also markedly decreases the strength.

2. Mixtures 1:1 by volume of cement and sawdust were reasonably strong; mixtures 1:2 were considerably weaker; mixtures 1:3 needed accelerators to have appreciable strength; and mixtures 1:4 were almost useless.

3. Pretreatment of sawdust is desirable. The most effective treatment is simply to boil the sawdust with water and wash. Acetone extraction has little benefit. Treatment of sawdust with a boiling potassium dichromate solution after a preliminary boiling with water gives a slight increase in strength. Boiling the sawdust with other electrolytes does not seem to be helpful. Boiling with ferric chloride has definite deleterious effects.

4. Addition of accelerating agents to the mixture makes the freshly prepared material much easier to handle and greatly increases the strength of the final product. Of the accelerators tested, Brocard's five chloride mixture is most effective.

Cement - sawdust mixtures might find application where great hardness and tensile strength are not required. The material might serve as a cheap filler or insulating material. The best preparation is to combine sawdust which has beenboiled with water, with cement, water and Brocard's five chloride mixture. The product exhibits a transverse strength of the order of 240 and the hardness of the order of 7000.

SECTION II

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SECTION III

The Effect of Soluble Compounds on Portland Cement

Abstract: The effects of a number of soluble substances on portland cement are observed. The action of hydrochloric acid on cement is studied in detail and discussed.

Introduction: In an effort to discover new uses for portland cement as a commercial product, it was decided to study the effects of various soluble substances on cement, concentrating on those reagents which tend to produce a gelatinous product. One objective of such a study would be to see if a portland cement product could be developed which would exhibit adhesive properties and could serve as a "glue" for joining materials such as slate, concrete, glass, metal, wood etc. Another objective of a study of chemical action on cement would be to determine if portland cement might find use as a chemical reagent in preparing useful products.

First, those electrolytes which tend to give a large volume to cement-water-pastes were studied. This investigation was based on findings by Brown(1) in his study of volume changes caused by the action of electrolytes on cement. The electrolytes were used in concentration which Brown found to give the greatest increase in volume to a given weight of cement. As the study progressed, the effects of other promising substances were investigated.

The substances whose actions were observed are: Calcium chloride, versene (sodium salt of ethylenediaminetetraacetic acid), aluminum chloride, formaldehyde, potassium ferrocyanide, ethylene glycol, glycerol, hydrochloric, acid and nitric acid.

Experimental: The effect of soluble substances on portland cement was first studied by mixing cement with a particular solution for a period of time and observing the nature of the paste formed. In order to do this it was necessary to set up a practical means of mixing. This was first attempted by mixing the cement paste in an open beaker with electrically driven paddle. To facilitate mixing, the beaker containing the paste was mounted on a freely rotating platform. This was an immediate failure because the paste soon set and stalled the motor. The next prodedure was to employ the same device but to attempt to slow the time of set by preventing evaporation of water. To accomplish this the surface of the paste was continually subjected to a stream of water saturated nitrogen obtained by passing nitrogen from a tank through two Mulligan gas absorbing bottles filled with water. This second method was an improvement but was not satisfactory. ~~and was~~ The procedure finally used. ~~This~~ consisted in putting the cement and solution in eight ounce gas bottles along with three or four glass marbles, stoppering the bottles firmly with rubber stoppers and placing the stoppered bottles on a ball mill where the bottles were rapidly turned causing the marbles to continually agitate the mixtures. Mixing could be continued in this manner for long periods of time without attention. With a few exceptions the cement paste did not set while being agitated on the ball mill.

At the beginning of each run, 20 grams of cement and 30 ml. of water were placed in the bottles. As the mixture grew thick small additions of water were made to keep the consistency at a point where mixing by the marbles would still be effective.

Unfortunately, no startling results were obtained with mixtures reacted in this manner at room temperature. Adhesive tests on paper, glass, and metal were almost complete failures. One significant observation was that with all the solutions tested the mixture on continued agitation lightened in color.

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Since lengthy reaction (up to one month of continued agitation) at room temperature failed to yield much significant information, reactions at elevated temperatures were studied. The action of several salts on portland cement were observed at elevated temperature (about 100°C) but here again no significant results were obtained. In a final attempt to find some reagent which would alter the physical properties of portland cement paste, the effects of mineral acids were studied. On addition of 100 ml. of 3N hydrochloric acid to 10 grams of portland cement, a series of significant changes was noticed on application of heat. The gray slurry of cement and water turned bright yellow and no trace of dark coloration or dark residue remained. The solution was trongly acidic. After boiling for one hour a flocculent precipitate started to form which slowly grew in volume. After one and one half hours of heating, the mixture was allowed to cool over night. After cooling, the product formed a yellow jelly. This was removed from the flask, placed on the mat of a Büchner funnel, and thoroughly washed with a dilute hydrochloric acid solution. The yellow color disappeared leaving a white semisolid material which proved to be silicagel.

A quantitative study of samples of 100 ml. acid and 10 grams of cement at room temperature showed that for concentrations of acid below two molar the sample was basic and colored dark gray and for concentrations above two molar the samples were acidic and yellow orange in color. At a concentration of two molar the cement - acid mixture was neutral (pH 7) and off-white in color. If this is taken as an "equivalence point" for the action of hydrochloric acid on cement, the "equivalent weight" of portland cement would be about 50 grams. An analysis of the silica gel obtained from the cement showed that 21.9 percent by weight of the cement was removed as silica by the hydrochloric acid treatment. (Excess of hydrochloric acid was used)

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It was found that the orange color imparted to the cement by hydrochloric acid showed several peculiarities. As mentioned above, the yellow color was easily washed out of the gel formed from the action of 3M acid. However, this was not the case with the yellow gel formed with 2½M acid. In this case the color could be removed neither by washing with water nor by boiling the yellow gel with water. The removal of the yellow coloration seemed to be dependent on the pH of the solution.

Tests with concentration nitric acid on portland cement showed results similiar to those observed with hydrochloric acid except that the gel was initially white instead of yellow.

Discussion of Results: Since observations on the actions of various soluble compounds on portland cement were not conclusive except for the action of mineral acids, this section will be limited to a discussion of the action of mineral acids.

Cement is known to contain silica in the form of silicates, tricalcium silicate being an important constituent of cement. The action of the mineral acid on cement might be postulated to occur:

$$3\ CaO\cdot SiO_2 + 6H^{+} = 3Ca^{++} + 3H_2O + 3\ Si\ O_2(gel)$$

TABLE IV

Typical analysis of Catskill regular portland cement. (Percent by weight)

SiO_2	23.50
Al_2O_3	4.60
Fe_2O_3	3.40
CaO	64.50
MgO	2.02

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Table IV (con't)

SO_3	1.35
Loss on ignition	0.50

Table IV gives information furnished by the North American Cement Corporation for the chemical analysis of a typical sample of Catskill regular portland cement. Silica is present in this cement to the extent of 23.50 percent. Hydrochloric acid treatment removed 21.9 percent of the cement as silica in the form of silica gel indicating that removal of silica by this method was about ninty three percent complete. With more elaborate procedure the separation should be quantatative.

Since iron is present in cement as the oxide, the yellow color ~~is~~ given to the gel by the action of excess hydrochloric acid is unduobtedly due to the formation of ferric chloride which is yellow itself. This is in agreement with the fact that with nitric acid no color was observed, ferric nitrate being colorless.

As noted before, when 100 ml. of 3M hydrochloric acid was added to 10 grams of cement a yellow gel was formed in which the yellow color was removed by washing the gel with very dilute hydrochloric acid. The yellow in this case was undoubtedly due to the formation of ferric chloride which is readily soluble in water and would be expected to wash out easily. On the other hand, this same treatment, differing only in that 2½ M hydrochloric acid was used instead of 3M, produced a similar appearing yellow gel in which the colored material was not removed at all by washing. In the presence of excess hydrochloric acid as in the first case there would be sufficient acid to react with all the lime etc. in cement and enough chloride left to keep the iron in the condition of free ferric ion i.e. ferric chloride. However, in the second case it might be postulated that the hydrochloric acid also formed ferric chloride in the early (over) part of the reaction but as the reaction progressed the basic constituents of the cement used up sufficient acid to cause the ferric chloride to revert to ferric oxide which being insoluble, was held in physical combination with the gel.

A silica-ferric oxide gel seemingly similar to the product described above was prepared and investigated by Holmes and Anderson,(2) Homles, Sullivan, and Metcalf,(3) and Holmes and Elder.(4) However, their gels were prepared directly from sodium silicate and ferric chloride. Holmes and Anderson, after preparing the silica-ferric oxide gel allowed the product to dry and then washed out the ferric oxide from the silica with dilute hydrochloric acid. When dried and activated, this latter product was found to contain all the capillaries expected from the removal of water and in addition a network of larger capillaries due to the removal of the ferric oxide. Holmes, Sullivan, and Metcalf describe in more detail treatment of the gel after dissolving the ferric oxide. Holmes and Elder state that such porous silica gel has found use in industrial processes in removal of sulfur compounds (and colored compounds) from petroleum, recovery of gasoline from still gases, and benzene from coke and oven gases, drying of air, oxygen, chlorine, acetylene, ethylene, carbon dioxide, and sulfur dioxide, and as a carrier for catalysts and a good adsorbent in taking up vapor in the vacuum refrigeration process.

It is possible that this mixed gel containing silica, ferric oxide, (and probably aluminum oxide also) might find satisfactory use as a catalyst for vapor phase catalytic cracking of petroleum hydrocarbons where similar compositions have been successfully used. (5,6,7,8) If satisfactory, a gel produced in this manner would be advantageous in that it would be cheap and easy to prepare in large or small quantities. Hydrated silica and hydrated ferric oxide represent acids and base respectively and the silica-ferric oxide gel might be an interesting adsorbent from this standpoint.

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SECTION IV

Mixtures of Portland Cement and Latex

Abstract: The nature of latex is briefly discussed. Studies on the coagulation of latex by portland cement indicate that mutual coagulation of oppositely charged particles seems to be the principal cause of coagulation.

Introduction: The study of mixtures incorporating latex with portland cement is a comparatively recent topic in the investigation of extended uses for cement. The industrial use of cement latex mixtures has received much study only in the last twenty years as is shown by the patent references for cement-latex compositions. The patent references indicate that the British are leaders in this field. Uses have been patented for cement-latex mixtures in flooring compositions (1,2,3,5,6,8,9), highway surfacing (2,8,9), wall coverings (6,7), pipes, baths, sinks, and molded articles (9).

Latex (10) is a milky fluid obtained from certain trees by cutting out a section of bark and collecting the exuded viscous fluid, latex. The principal source of latex in the tropical tree "Hevea braziliensus" grown in Brazil, Malaya, and the Dutch East Indies. Native latex is an aqueous suspension of rubber hydrocarbons with a particle size in the range of 0.5 to 3.0 microns in diameter. The suspension consists of about 35 percent by weight of hydrocarbons, 2 percent natural proteins, and small amounts of resins, sugars, and inorganic salts. The stability of the suspension is strongly affected by the pH. The suspension is stable at high or low pH values but is unstable in the range of about pH6 to pH3. Above the isoelectric point (which is approximately pH4.5 to pH4.8) the particles bear a negative charge and below the isoelectric point the charge is reversed. Freshly collected latex has a pH of about 7 and is stable but on exposure to air, coagulation takes place in a few hours due to the lowering of the pH by bacterial action. Thus in order to preserve latex as a stable suspension it is necessary to use a stabilizing agent. For this purpose alkaline materials such as borax, sodium or potassium hydroxide may be added to prevent this acid bacterial action. However, 0.5 to 1 percent by weight of ammonia has been found to be the most suitable stabilizing agent.

For the successful use of latex with cement additional stabilizing ingredients are also necessary. Stabilizing agents which have been patented for use with latex-cement compositions include: metaphosphoric acid ions (11), sodium silicate (12,13), casein (12,13,4), saponin (12,13), Igepon T (12,13), soaps (4), caustic soda (4,14) and alkali carbonate (14). It has also been found that vulcanizing agents for the latex are often desirable. (9,13,14,15,16,17).

The opportunities for research on cement-latex compositions are many. Since a search of the literature failed to show that any investigation had been done on the elementary problem of the direct action of portland-cement on latex stabilized with ammonia only, this topic was selected for further study.

Experimental: In this investigation of the cause of coagulation of latex by cement, mixtures of regular portland cement from the Catskill plant of the North American Cement Corporation and ammonia stabilized latex sample "NC 356 Latex, Cont. 38006, TS 67.36%" donated by the Naugatuch Chemical Company were used.

As a preliminary experiment, portland cement and the latex were mixed directly. This resulted in the formation of a spherical shaped rubbery mass which when allowed to stand for a few days proved to consist of small lumps of cement held loosely between sheets of rubber. When the rubbery mass was deformed, coarse particles of cement fell from the material. The product was weak and heterogeneous in composition.

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Next, a quantitative determination of the coagulating effect of cement on latex was made. An accurately weighed sample of about one gram of latex was diluted with 50.0 ml. of distilled water. The diluted latex strongly resembled milk in color and opacity. With constant stirring, dry cement was slowly added to the diluted latex until all the latex had been coagulated by the cement. Coagulation was presumed to be complete when the filtrate of the supernatant liquid became clear. It was found that about 12.8 grams of cement was sufficient for coagulation of 1.00 gram of latex from sample NC 356. These experiments clearly showed that additional stabilizers as necessary if a workable product is to be obtained.

As an hypothesis for the cause of the coagulation of the latex by the cement, it was proposed that the electrolytes resulting from the solution of certain constituents of the cement, most likely the calcium ion from the lime, were responsible for coagulating the latex sol. This hypothesis is in accordance with the Schultz-Hardy rule of coagulation (18) which states that the effective ion in precipitation of sols by electrolytes is the ion opposite in sign to the charge on the colloidal particles and that the precipitating power of the effective ion increases greatly with increased valence of the ion.

To test the validity of the assumption, the following experiment was devised. A slurry was prepared of 100 g. of portland cement and 200 ml. of distilled water. The electrolytes dissolved from the cement were separated from the slurry by filtration, first through ordinary filter paper, then through a fine fritted glass crucible. The final filtrate was perfectly clear and had a high pH (about 11). The filtrate was slowly added with constant stirring to a one gram sample of latex diluted with 50 ml. of distilled water. There was a small amount of coagulation of the latex but even when all the filtrate had been added, the latex sol was still opaque and showed little visible evidence of change.

Thus it seems definite that electrolytic coagulation is not the principal contributing factor to the coagulation of latex by cement. The dissolved electrolytes from slightly less than 100 g. of cement failed to cause appreciable coagulation of an amount of latex completely coagulated by 13 grams of cement.

Since the first hypothesis proved to be inadequate, it was proposed that mutual coagulation by particles of opposite electrical charge was the cause of the coagulation action. From the literature (10), latex at a high pH i.e ammonia stabilized, is said to have a negative charge. Therefore a simple arrangement was set up to prove that this was true for the particular latex sample NC 356.

A one gram sample was diluted with 100ml. of distilled water and placed in a 250 ml beaker. Two polished platinum electrodes were inserted in the dilute latex and were connected to a six volt storage battery. The effect of the passage of current through the sol was observed. The negative electrode (cathode) remained perfectly clean and shiny but the positive electrode (anode) soon became covered with a white deposit of rubber. This would seem to indicate that the latex particles were negatively charged. However, an examination of the solution immediately surrounding the anode showed that the pH was considerable lower than the main body of the solution. This lower pH would be expected as a result of some electrolysis of the water at the anode by which the hydroxyl ion concentration is considerably lessened causing a pH drop. Since the lowering of the pH of a latex sol is known to cause coagulation it was thought possible that the anodic coagulation was a result of the acid action rather than the result of the charge on the particles. Therefore, another arrangement was devised to determine the charge on latex particles. A cell was fashioned from a microscope slide as shown in diagram A.

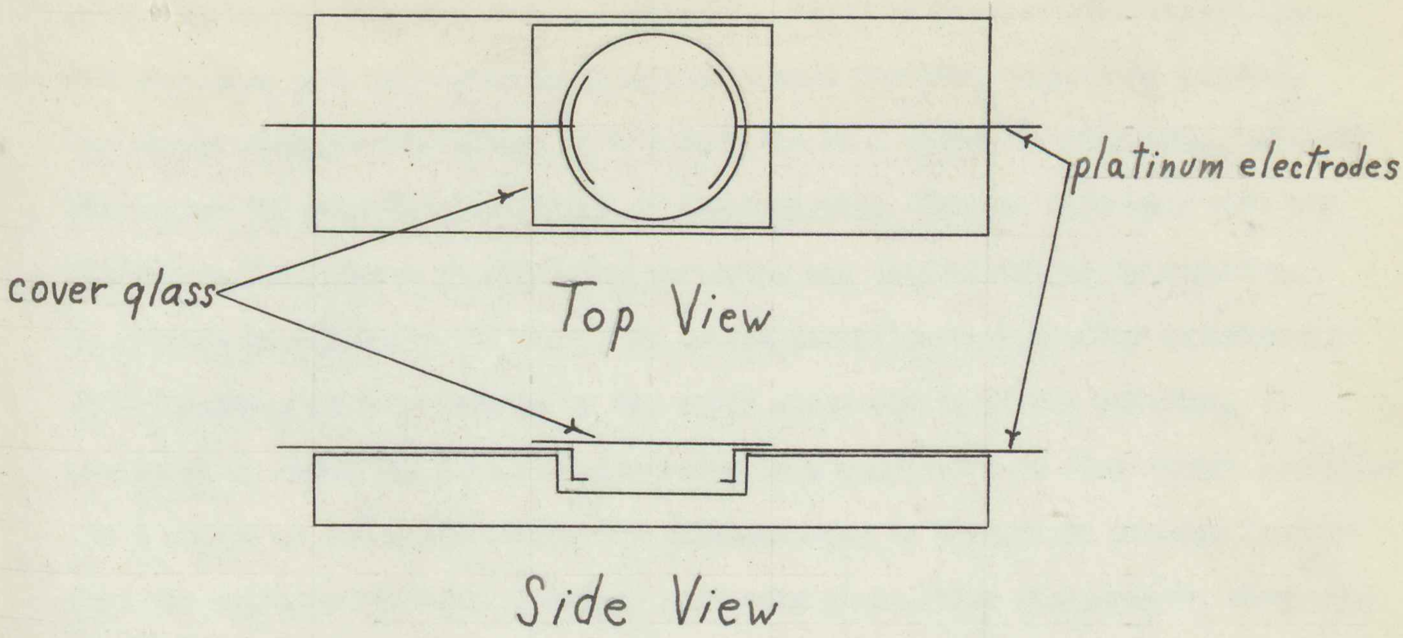

DIAGRAM A

A very dilute suspension was prepared (1 drop in 500 ml. distilled water); some was placed in the depression of the slide and the cover glass was affixed. The slide was placed on the stage of a microscope and the movement of particles in the cell was observed. Cross illumination using a Tyndallometer as a light source enabled the movement of the near colloidal sized particles to be observed as moving specks of light. Uninfluenced by electrical forces the particles drifted sluggishly across the field (probably convection effects). By means of six volt storage battery and a two way dipole switch connected to the electrodes, current was passed through the cell first one way, then the other as the polarity of the electrodes was reversed with the two way switch. Under the influence of the electrical attraction the particles moved toward one electrode. (The optical reversal of motion in a microscope field wa s taken into account.) When the polarity of the electrodes was reversed, the direction of the movement of the particles likewise reversed sharply. Repeated observations showed that the particles were consistently attracted toward positive electrode (anode). The abrupt change of direction of the particle on a change in electrode polarity eliminates the questionable effect of electrolysis. Thus in agreement with the literature, the charge on the latex particles was determined to be negative. An attempt to determine the charge on cement particles by a similar experiment failed because of interference by the rapid electrolysis of the solution. It was found by immersing platinum electrodes in a suspension of fine cement particles in a beaker of water and connecting the electrodes to a six volt storage battery that the positive electrode remained perfectly clean while the negative electrode soon became coated with a gray material (cement particles). This was taken as evidence that cement particles bear a positive charge.

Discussion: As explained before, the assumption that coagulation of the latex by cement was caused by the effect of electrolytes was proven to be incorrect. The fact that latex is stable at a high p^H might offer an explanation for the failure of the strongly basic solution containing calcium ion to effect coagulation. From the limited observations outlined above, there is evidence that the second hypothesis concerning mutual coagulation by oppositely charged particles is valid. It is believed (19) that mutual coagulation is caused by the mutual discharge of electricity between oppositely charged particles with subsequent agglomeration of the particles into clumps. Thus positively charged cement particles in contact with negatively charged latex particles would effect in this manner mutual discharge and agglomeration.

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SECTION V

CEMENT – PLASTIC COMPOSITIONS

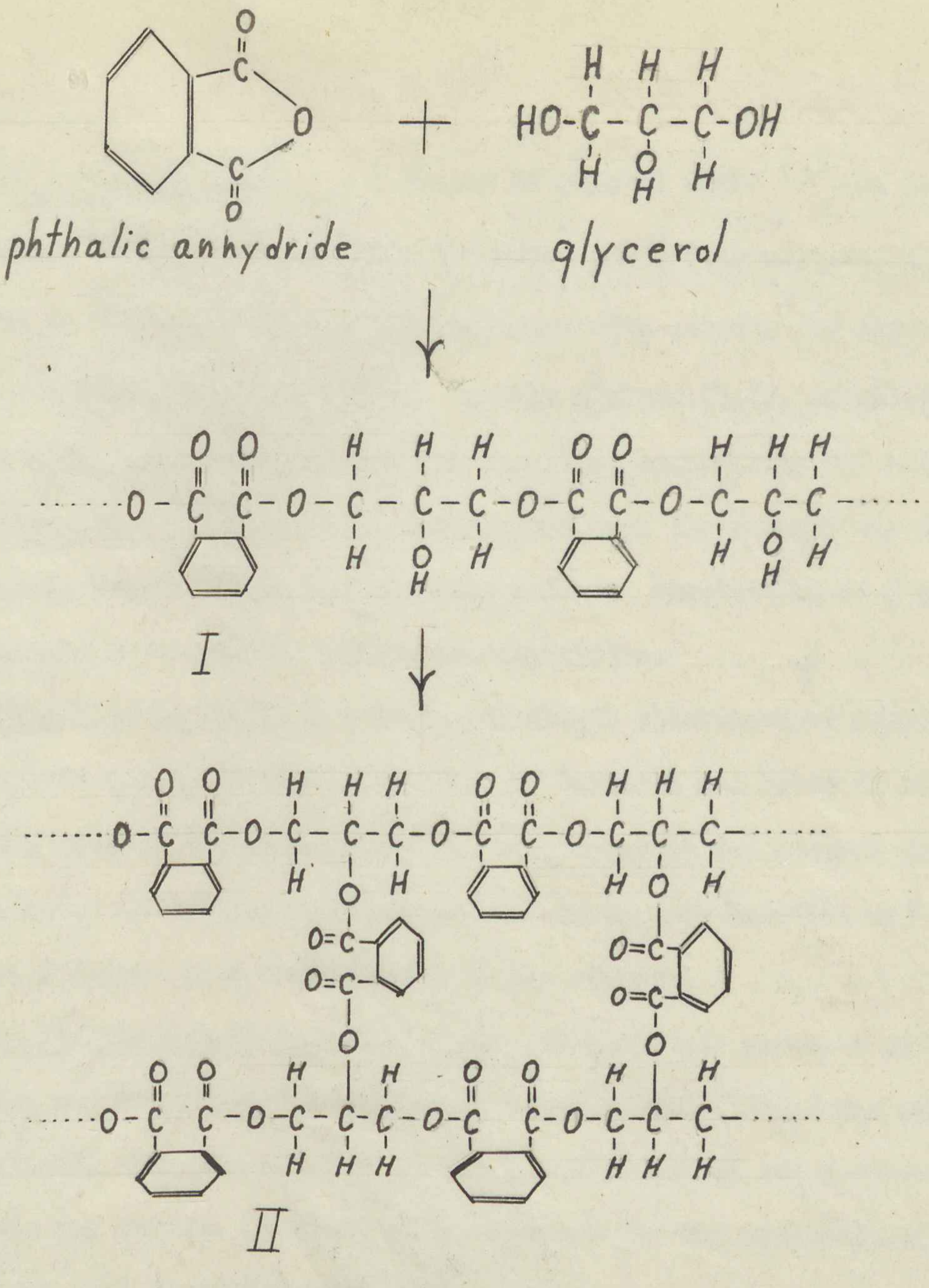
Abstract: Five samples of portland cement and alkyd resin are prepared under different conditions and the physical and chemical properties are compared.

Introduction: The incorporation of synthetic resins or plastics in portland cement compositions was another attempt to expand the usefulness of portland cement. Such compositions might combine to advantage the properties of cement and plastic e.g. strength, flexibility, resistance to chemical action, cheapness, lightness, ease of working. Since time for this phase of the study of further uses for portland cement was limited, it was decided to study compositions of portland cement with (1) alkyd resin and (2) an alkyd resin modified with fatty acid.

Alkyd resins(1) are condensation products of polybasic acids or anhydrides and polyhydric alcohols, hence the name alkyd (alcohol + acid = alkyd). The most common member of this group is the resin named glyptal, formed from the condensation of glycerol with phthalic anhydride and this was used in the study of portland cement with alkyd resins.

The resinification process consists of the esterification of phtholic anhydride and glycerol into a large three dimensional structure. The mechanism of resinification has been proposed by Carothers (2) to take the place in two stages. First a linear polymer I is formed by esterification of the α-hydroxy groups of the glycerol. This is then followed by a crosslinking of the chains through the esterification of the remaining hydroxy group with phthali anhydride to form the three demensional structure II.

SECTION V



Alkyd resins are often modified in order to give specific properties. Typical modifying agents are drying and non-drying oils, fatty acids, natural or synthetic resins. It was decided to study the effects of modification of an alkyd resin with a fatty acid, linoleic acid, in cement - plastic compositions. Resins modified with fatty acids tend to be more soluble and flexible.

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Experimental:

Cement - Plastic Sample A - A sample of glyptal resin (3) was prepared by heating a mixture of $\frac{1}{2}$ mole of phthalic anhydride and $\frac{1}{3}$ mole ofglycerol. The sample melted at 132°C and heating was continued with stiring for one hour at which time the temperature was 183°C. To this mixture 37.5g. of portland cement was added with thorough mixing and the resulting composition was poured into a mold to cool. After standing for several days the product was dark gray, smooth surfaced, very brittle, and slightly sticky. Examination of a cross section showed the sample to be fairly uniform in composition.

Cement - Plastic Sample B - Since the slight stickiness of sample A indicated incomplete resinification, a portion of sample A was baked in an oven at 150°C for two hours. The composition was thermoplastic and assumed the shape of the container. On cooling, the product was hard, very brittle, and not sticky. Numerous depressions were visible on the surface.

Cement-Plastic Sample C - Another glyptal resin was prepared as in sample A but heating was continued for two hours. More cement (130g.) was added to the hot plastic than was added in sample A. When cooled the product was hard, brittle and uniform in cross section except for the inclusion of a few air bubbles. The composition was not sticky.

Comparison of samples B and C -An attempt was made to find further information on the reaction of dissolving the plastic from the cement with acetone. Three gram samples of B and C were each put in a test tube, 15 ml. of acetone was added to each, and the tubes were stoppered and shaken. Likewise plain cement and acetone were placed in a test tube which was stoppered and shaken. After several hours the test tubes were compared. The plain cement in acetone remained the gray color of unreacted cement. Sample C with acetone was gray but somewhat lighter in color. Sample B with acetone was quite light in color with a tan hue. The three test tubes were then centifuged. The plain cement and acetone showed a gray sediment. Sample B and acetone showed a sediment of a lower gray and an upper white layer. Sample C and acetone showed a sediment of a lower dark gray and an upper light gray portion. The supernatant acetone was decanted from the samples in the test tubes and fresh acetone was added. After one day the plain cement and acetone was dark gray with a brownish cast and consisted of fine particles. Sample B and acetone was very light gray, almost cream colored with coarse particles. Sample C and acetone was light grey with coarse particles.

Cement - Plastic Sample D - A sample was prepared using an alkyd resin modified with the fatty acid, linoleic acid. A mixture of 27 g. phthalic anhydride, 15 g. glycerol, and 26 g. linoleic acid, was heated and stirred for one hour at which time the temperature was 197°C. On cooling, the plastic was a homogeneous, clear, dark brown mass which was very sticky and stringy. To the cooled portion, a paste of portland cement (150 g.), water and 2g. calcium chloride as an accelerator was added and thoroughly stirred. The resulting composition was heated in a 150°C oven for one hour to further the polymerization of the plastic. On cooling, the product resembled a cement - water mortar in color. The surface was easily scratched with a fingernail where as samples A, B, and C were not. Sample D differed from Samples A, B, and C in that it had a crumbly rather than a brittle nature.

Cement - Plastic Sample E - A sample was prepared of 100g. portland cement, 17g. water, 33g. phthalic anhydride, and 22 g. glycerol. In contrast to the previously prepared samples, the cement and raw materials of the plastic were mixed together before reaction. After sixty five hours at room temperature, the product was firm and very dark gray on the surface. It could easily be marked with a fingernail. Lumps of white material, 1-2 mm. in diameter, were dispersed through the mass. The samples on being heated in a 120°C oven for five hours became covered with a soft white material but otherwise there seemed to be little effect. The sample was then heated in an oven at 160-170°C for five hours. As a result of this heating the material looked and felt pitchy and was light in weight. On being cut open (with some difficulty) the interior was gray and filled with cellular type air spaces. A number 8 nail was pounded into the sample. The sample offered moderate resistance to the introduction of the nail and hung quite tenaciously to the nail once it was in.

Discussion: By dissolving, with acetone, the plastic from samples B and C and observing the physical characteristics of the remaining cement, it appears that there was some reaction between the cement and plastic and that the reaction was more extensive in sample B. As discussed in section 3 on the effect of soluble substances on portland cement, the reaction of cement with a soluble substance is generally characterised by a lightening of color. The fact that samples A and B with acetone were lighter than plain cement is indicative that some reaction occurred. The lighter color from sample B indicates further reaction than in sample C. This would be expected since sample B was heated for a longer time than sample C. However, the reaction of the cement does not seem to be extensive in any case and the main function of the cement is probably as a filler. Sample E shows evidence that adding cement to the preliminary product and having the cement set before heating cause a marked change in the nature of the final sample. The air spaces are probably the result of the action of steam from the excess water (on heating) or from the reaction of phthalic acid with the basic constituents of cement. The ability of sample E to take and to hold nails is probably a result of the porous nature of the product.

Summary: The results obtained from the preparation of the five cement-plastic samples show that if in a cement-alkyd resin composition, the resin is allowed to form before addition of cement, the product is dense and brittle in contrast to a composition in which the cement is allowed to set before the resinification process begins. The latter composition is light, porous, and more flexible. Modification of the alkyd resin with fatty acid seems to have little benefit, causing the material to be weak and crumbly.

SECTION V

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