AN ATTEMPT TO IMPROVE CERTAIN PHYSICAL AND CHEMICAL PROPERTIES OF CONCRETE THROUGH THE USE OF VARIOUS ORGANIC POLYMERS

by

Robert Lehrer UC 1956. U C

A thesis presented to the Department of Chemistry of Union College in partial fulfillment of the requirements for the degree of Bachelor of Science with a Major in Chemistry.

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Approved by Charles B. Hurd

Date: June, 1956

ACKNOWLEDGEMENT

This thesis summarizes the research conducted during the period from June, 1955 through June, 1956. This research was supported by the Research Fellowship established in 1948 in the Department of Chemistry of Union College by the North American Cement Corporation.

The author wishes to acknowledge here, with much thanks, the aid and advice of Dr. Charles B. Hurd, under whose direction the research was carried out at the College, and that of Messrs. H.F. Kichline and D.F. Nordquist at the Catskill, N.Y. plant of the North American Cement Corporation

INDEX

INTRODUCTION

Portland cement as we know it, was discovered during the nineteenth century, though cement itself was known for uncounted centuries before this. With the advance of the Machine Age, the production of this substance, one of the most basic of all building materials, has increased tremendously. In our rapidly advancing era, this material has found many new and varied uses-- in industrial and domestic construction, in the marvelous engineering projects we know as bridges and super highways, and, of course, in the laying of durable concrete floors and sidewalks. But even in this age of ours, noted especially for its scientific progress, no way has yet been found to prevent, effectively, the weathering, spalling and other types of corrosion from eventually ruining the concrete structure.

Our work of the past year has been one of many attempts which both have been and will be made to correct this unfortunate situation. Through the incorporation of various organic polymeric substances into several kinds of concrete mixes, we have attempted to produce a mixture which offered more than the usual resistance to corrosion by water and acid. In addition, we have noted the effect of the various additives on the physical properties of a normal mixture of cement, sand and water. In doing this, we sought a worthwhile property change toward simulation of a mortar cement mix, as exemplified by the Blue Bond product of the North American

Cement Corporation.

This thesis will show the history of this type of work, our experimental procedures and apparatus, and an evaluation of the results obtained during the year.

ABSTRACT

The historical background for the project is discussed as an introduction. A description of the preparation for and the planning of the work is followed by a discussion of techniques; reasons for the changes in method of acid testing are outlined and the modified procedure discussed. Variations in acid tests are described. A new type of experiment, utilizing a "continuous flow" apparatus is discussed. A description of our attempts to convert the incorporated resinous material to its final stage of polymerization is given. The field of organic polymers is discussed using the literature, and the procedures followed in securing and testing these materials both qualitatively and quantitatively are described. The experimental results are tabulated and evaluated, and the year's work summarized.

HISTORICAL AND GENERAL INTRODUCTION

The literature of chemistry since the start of this century, as shown in panoramic form by Chemical Abstracts, is filled with accounts of attempts to improve the acid and water corrosion resistance of concrete through the use of additives. The limitation of space and the question of its value to this thesis prohibit a more complete treatment of the enormous amount of literature to be found on this subject, but we cite as typical examples among very many others, the work of Haddan (1) in England in 1909, of Splittgerber (2) in Germany in 1920, of Frank and Dietz (3) in the United States in 1931, of Sorkina (4) in Russia in 1939, of Brick (5) in the United States in 1951, and of Suzuki (6) in Japan in 1953.

All of these men developed what they thought to be a waterproof or acid resisting concrete by the addition of either inorganic or organic materials to Portland cement, sand and water mixes. It is indeed rather surprising that one finds, in the literature of Portland cement additives to date, very little reference to the newest and most rapidly growing field of organic chemistry-- that of resins and plastics. We believe that this field of study offers the most promise for a solution to the corrosion problem, and therefore deserves a good deal more investigation than has thus far been carried out.

The work that was done at Catskill several years ago deserves mention here. Reference is, of course, to the large number of charts listing results of tests made at Catskill on concrete containing various types of additives, including some resins. This work was done, according to the charts, starting around the year 1910. The data recorded are for setting times and compressive and tensile strengths. No acid tests were performed on these specimens, however, and this work differs from the present study in that respect.

The research work done by Brown (7) in 1950 and Dunbar (8) in 1955, both at Union College, shed some light on certain phases of our work this year. Brown's experimentation with several of the constituents of some of the resins we have used showed, by means of hydration tests, the resulting changes in volume to be expected with the setting of cement. The changes, as compared to a standard mix, were caused, of course, by the addition of foreign materials of various types to cement and water. This work was continued and projected to a large degree, by Dunbar. As an introduction tothis type of test, several of these hydration tests were carried out this year, but on a much more limited basis than was used by either Brown or Dunbar. In 1955, Dunbar worked with other additives also, in actually pouring concrete blocks containing these additives, and ascertaining quantitatively the corrosive effect of certain acids on slabs cut from these blocks. The effect of these added materials on the compressive strength of the concrete was determined at the Company's Catskill plant.

This year we modified greatly in several respects, some of the tests and procedures Dunbar had been using. First of all, we increased the scope of the work in order to cover as many different resin kinds as we found available to us. Then, in addition to seeking an agent for improving water and acid corrosion resistance, we were continually on the watch in the mixtures with which we worked, for the appearance of desirable properties as evidenced in the Blue Bond mortar cement of the company. Finally, much of the experimental procedure used in previous years was improved to the point where it simulated actual conditions rather than created artificial conditions never encountered in the practical use of cement.

A necessary preliminary to actual laboratory work was a detailed study-- first of cement and its properties; and then of the various resin types, uses and properties, and forms available. For this study, the following authors were of much help and will be referred to again later: Bogue (9), Mason and Manning (10), Simonds (11), and Richardson and Wilson (12). Much of the information we have used in our work has come from the Modern Plastics Encyclopedia Issue (13) of September, 1954. Of special interest was the Plastics Properties Chart found in that issue. Chemical Abstracts and publications such as Chemical and Engineering News and Industrial and Engineering Chemistry all were used to a large extent to keep up with the present published work along these lines.

What we present here is, by no means, a complete picture, for the field of organic polymers is almost limitless, and the variations within each type are staggering to imagine. Our work this year, however, has been at least a good beginning to a project which is worthy of several years study.

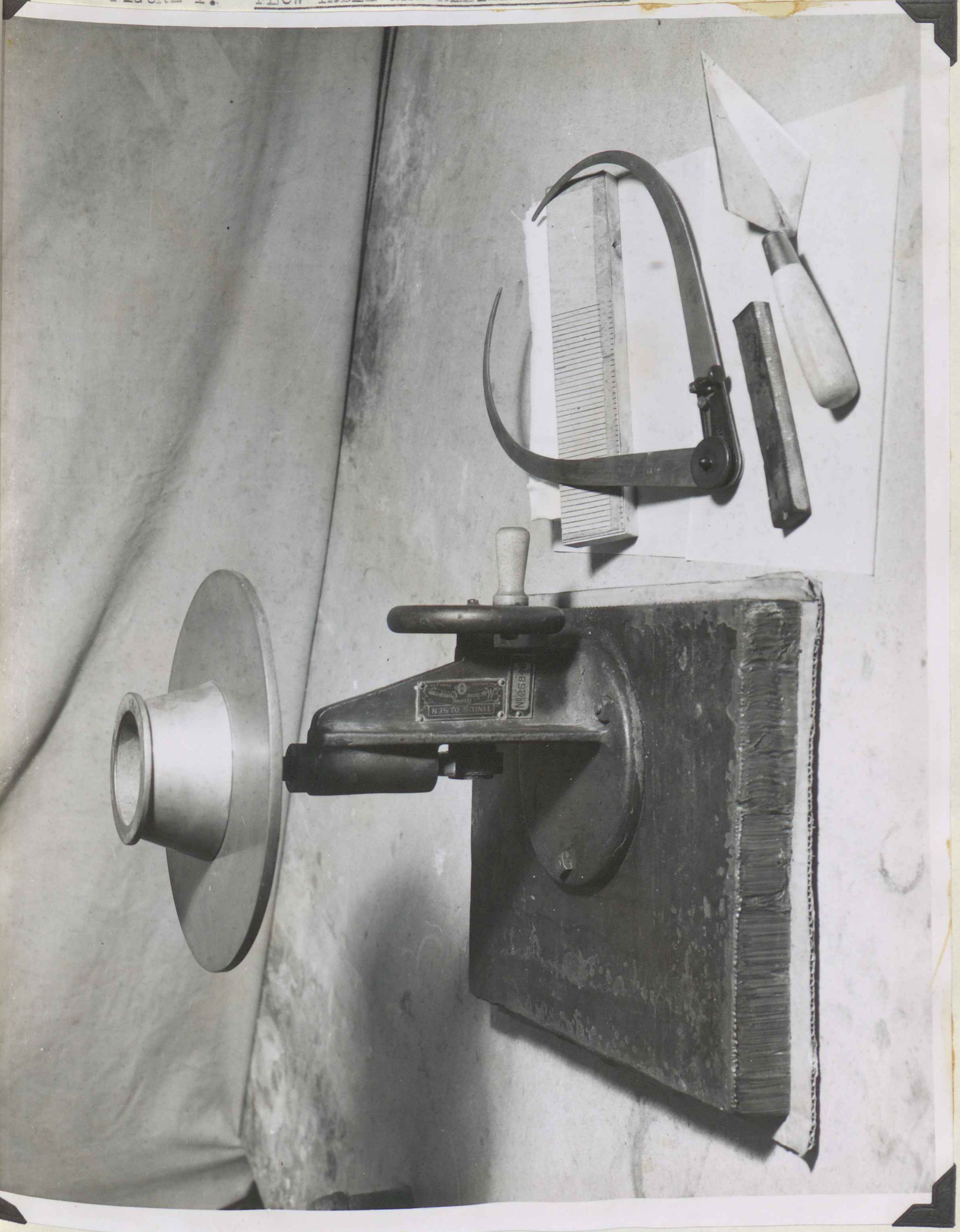
APPARATUS AND PROCEDURE

Preparation and Plans

Early in the summer of 1955, one full day and parts of several others were spent at the Catskill plant of the North American Cement Corporation. This time was taken up by a tour of the plant and instruction in the basic laboratory procedures followed in quality control, some of which were to be used in our work at the college. At this time also, the project for the year was discussed and partially planned. It was to consist of the making of blocks using regular Portland cement plus additives, and the testing of these blocks for compressive strength at Catskill and for water and acid resistance at Schenectady. Acid tests also were to be made on samples of the company's Anti-Bacterial Cement (ABC) and Blue Streak Air Entraining Cement (BSAE). A special mixture of Blue Bond mortar cement was given to us. This special mixture lacked the plasticizer necessary to impart to it the desirable properties of a mortar mix; it was suggested that we attempt to find a suitable plasticizer to add to this material in order to better the company's present Blue Bond product. Another suggestion at this time was that we try to use the new "silicones" in our work.

A flow table (photograph, Fig. 1) was brought back to Schenectady from Catskill. The use of this instrument modified a procedure which had been followed at Schenectady in previous years. It had been assumed that a "normal" cement, sand, water

FIGURE 1. FLOW TABLE and ALLIED APPARATUS



mix could be achieved every time by using 500 grams of Portland cement, 1375 grams of Ottawa graded sand, and 250 milliliters of liquid (water plus additive in solution). This assumption was erroneous, since the flow properties are subject to change with each batch of cement and, of course, with the addition of various additive solutions. The flow table, use of which is described here later, and more completely in ASTM Standards on Cement (14), gave a quantitative measure of flow, and put our concrete block making on a comparative basis with that used in industry.

The Pouring of Concrete Blocks and Cubes

During the early part of this year's work, the method used for making concrete blocks was as follows: After weighing out on the laboratory balance 500 grams of Portland cement and 1375 grams of Ottawa graded sand, 250 milliliters of water or of water plus additive in solution were placed in the dry, porcelain clad mixing bowl. The cement was added to the liquid, and mixed for 30 seconds, the hands being protected by a rubber glove. Then, approximately one half of the testing sand was added and mixed for 30 seconds. Finally, the remainder of the sand was added, and mixing was carried out for 1½ minutes, by vigorous and continuous kneading and squeezing. This mix was then poured into one of the 2"x2"x12" greased molds in the gang mold, tamped in in the standard manner using a rubber tamper, covered with a glass plate and a damp cloth, and allowed to set. Blocks containing Melmac 480 (melamine formaldehyde product of American Cyanamid Company) in percentages varying from 0.01% to 1.00% by weight of the cement were made in this way. Also, with proportionately less amounts of materials and with smaller individual molds, but using the same method, we made 1"x1"x6" blocks, some containing only Portland cement with no additives, some containing 0.2% Sodium Methyl Siliconate (use of which in our work was discontinued), and one containing 0.01% Melmac 480. All of these blocks were sent on to Catskill to be tested for their strength. The results of these strength tests, together with others, will be presented later with appropriate comment in the section entitled Experimental Results.

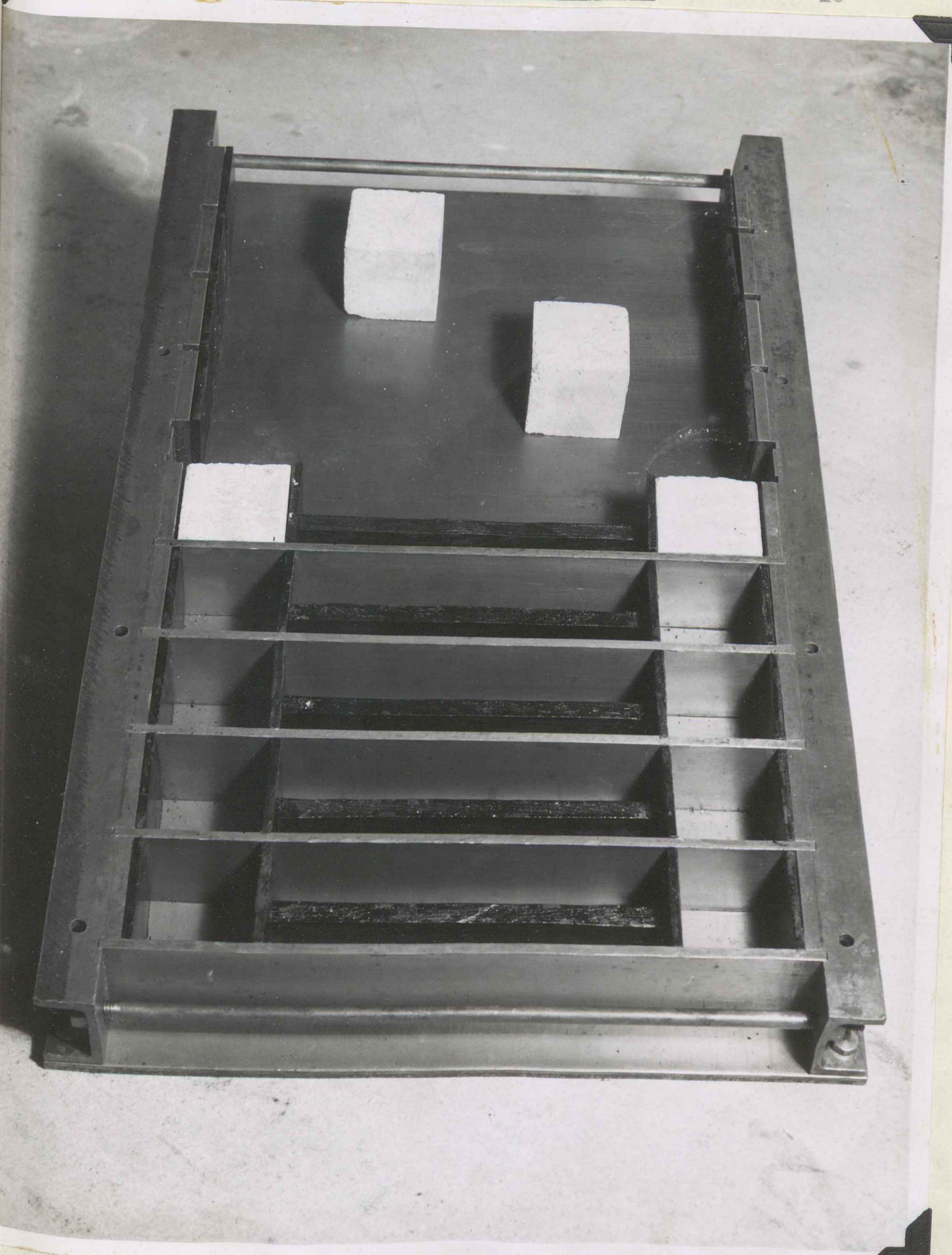
The above procedure was used before we were introduced to the flow table. Of course, the procedure was modified to conform to ASTM standards once we had a flow table at our disposal in Schenectady. The modified procedure was as follows: After weighing out the cement (500 grams) and sand (1375 grams), a volume of liquid (water or additive solution) was placed in the mixing bowl. The exact volume to be used depended upon the flow test which was to be given the resulting mix. The cement and sand were added in exactly the same way as described previously. Then, a layer of mortar about 1" thick was placed in the flow mold (truncated cone pictured in Fig. 1) and tamped 20 times with the rubber tamper. The mold was then filled with mortar and tamped again. The mortar was then cut off to a plane surface flush with the top of the mold by drawing the straight edge of our trowel across the top of the mold with a sawing motion. The mold was lifted away from the mortar 1 minute after mixing had been completed. Immediately, the table was dropped 25 times in 15 seconds; that is, the table top was lifted up and let down by means of turning the handle on the machine, so that the truncated cone of mortar was flattened out. The flow was the resulting increase in average diameter of the mortar mass over its original 4", expressed in terms of percentage of the original diameter. A flow of 100%, for example, represented a final diameter of 8". This diameter increase was measured using the calipers and scale shown in Figure 1. A flow of from 100% to 115% was acceptable, though the closer to 100%, the better the mix. If the flow of the mix fell between the prescribed limits, it was usable; and, after remixing the part of the mortar used in making the flow test with the remainder of the mix, blocks were immediately poured. If the flow fell outside of the limits, the mortar was discarded and a new volume of liquid tried with a fresh mix. Using this method, we poured 2"x2"x12" blocks containing percentages of Melmac 480 varying from 1% to 10% with an amount of Sodium Hydroxide found necessary to keep the Melmac in aqueous solution in each case; other blocks were poured containing the same amounts of Sodium Hydroxide, but without the Melmac 480; others containing from 1% to 5% of Dimethylol Urea, a urea formaldehyde resin; still others were poured using Anti-Bacterial Cement alone and in combination with Portland cement. All of these blocks, like the others made using the old method, were tested for strength at Catskill, and the results will be presented under Experimental Results later.

Concrete Cubes and Our Numbering System

For acid corrosion tests (see later section), Dunbar (8) had used 2"x2"x1" slabs cut from 2"x2"x12" blocks at Catskill on the masonry saw. We decided that the sawing might introduce an artificial strain on the concrete surface and would consequently give erroneous results. Therefore, we used in our acid tests, only 2"x2"x2" cubes which had been poured as such either in Schenectady or at Catskill. At Catskill, metal molds were available for making these cubes, but since we had none of these molds at the college, we fitted our large gang mold with 2"x2" squares of tempered masonite on either end of each individual mold (photograph, Figure 2). This enabled us to make a maximum of 18 2"x2"x2" cubes at one time. The procedure followed in pouring all of the cubes which we made in Schenectady is the same modified method used in making the longer blocks. The cube making at Schenectady was discontinued after a later conference, when it was decided, for the sake of uniformity, to leave this task to Catskill. Before this conference, however, cubes were made at Schenectady which contained Portland cement with no additives (used as the standard for comparison), and with the same concentrations of Melmac 480 plus NaOH and of NaOH alone which had been used previously in the longer blocks that were sent to Catskill for strength tests. A description of the results of acid tests on these cubes is found in the section of Experimental Results.

In order to prevent any confusion of identity of the

FIGURE 2.. GANG MOLD FITTED FOR CUBE MAKING



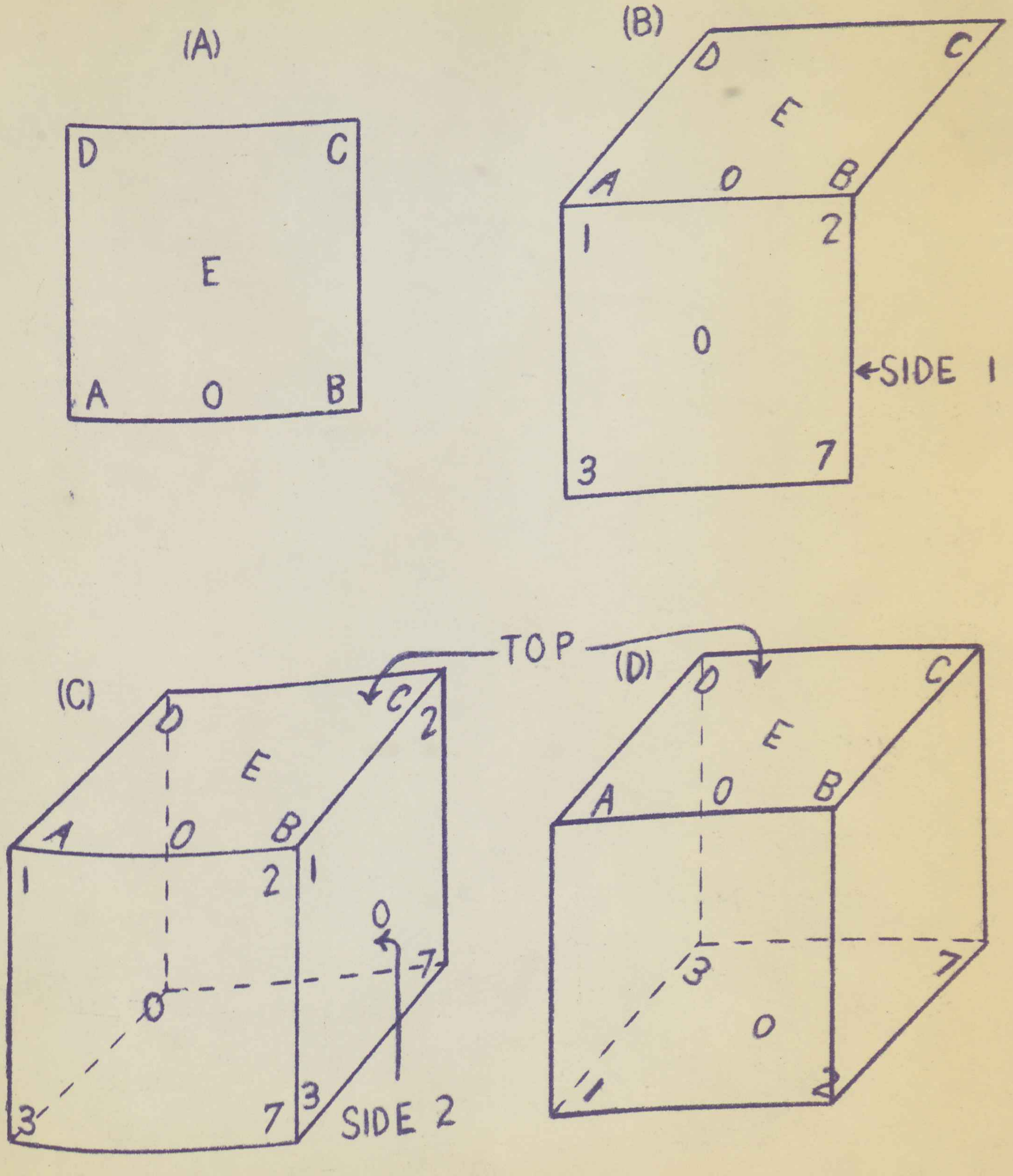
various cubes during the testing in Schenectady, some sort of numbering system was found to be advantageous by Dunbar. The system as he devised it, however, was limited as to the quantity of cubes to which it could be applied. A modification was therefore made, and the numbering system we used during the past year could have been applied to a maximum number of 50,000 cubes.

Reference to Figure 3 will help to clarify the following explanation of our numbering system.

The "top" of the cube is always the surface opposite the trowelled surface (the "bottom"). It is divided into 6 lettered sections or areas, as indicated in Figure 3a. Every cube will have one hole drilled in the "O" position of the top indicating, since this is the only surface on which there is an "O" position, that it is the "top". The letters "A","B","C","D", and "E" we have used to represent the days of the week, Monday through Friday, Saturday having no letter designation. The purpose for this was to make it easier to tell at a glance, the cube's composition, since the letter, in essence, represented the date of pouring, and our card file on these cubes summarized briefly the pouring date and contents. Side 1 is the side of the cube which is directly adjacent to the "A" "O" "B" areas of the top, and like the four remaining faces, will be divided into 5 areas, numbered as shown in Figure 3b. Using combinations of these 5 numbers, any number from 1 to 9 may be represented by the holes drilled in the cube face. Side 2 is that side adjacent to side 1 in a counter-clockwise direction; side 3 is directly

FIGURE 3

CUBE NUMBERING SYSTEM



opposite side 1 and side 4 is directly opposite side 2 as shown in Figure 3c. The "bottom" (trowelled surface) was usually not used since it was the acid action on this surface in which we were primarily interested. However, if necessary, the bottom could be used to designate series. Figure 3d shows the correct perspective for reading the bottom face. All holes were drilled carefully about ¼" deep using a power drill press equipped with a drill designed for boring into concrete.

Acid Tests

Dunbar (8) immersed slabs of concrete, 1"x2"x2", cut from large 2"x2"x12" blocks, in solutions of Hydrochloric, Acetic and Lactic acids of concentrations 0.5%, 1.0%, 2.0%, and 5.0% for 1 day, then 2 days more, then 7 days more, then 10 days more, making a total of 20 days immersion. These slabs were dried out at 105 degrees Centigrade in an oven before the first and before every subsequent weighing. After each exposure to acid then, the slab was washed in water, scrubbed with a cocoa fiber brush to remove loose particles, dried in the oven and weighed, and the solution of acid was changed at the end of 1 day, 3 days, and 10 days.

Several disadvantages were inherent in this procedure. As mentioned previously, the cutting of 1"x2"x2" slabs from larger blocks might introduce artificial strain on the surface; we therefore used 2"x2"x2" cubes poured as such, for all of our acid tests. An important acid used very frequently in the cleaning of concrete floors, phosphoric acid by name, was not one of those used previously. We therefore added this acid to the list, thus making four acids usable for these acid tests.

Twenty days seemed excessively long, and this period of time for immersion was cut down to 15 days, since it was assumed that this would give just as complete a picture as did the twenty day duration. The practice of drying the blocks out at elevated temperature was very artificial, and did not at all simulate actual conditions. Also it was well known that the heating of the blocks before weighing left them dry before being again placed in acid. The dried out condition allowed water containing acid to soak into the blocks, and therefore more acid corrosion was evidenced than would have been had the blocks not been dried out. This practice of drying at elevated temperatures, therefore, was discontinued. A study of pH changes in the acids during the corrosion tests (see Experimental Results) showed that the acid was being used up more quickly than it had been assumed, and therefore, the acid solution was freshened at more frequent intervals during the 15 day duration of tests.

A summary of the modified test procedure used, then, follows: The 2"x2"x2" cubes, after curing in water overnight, were scrubbed with the cocoa fiber brush under running water, rinsed and surface dried with a towel, allowed to stand in air for 15 minutes, and weighed. They were then placed in 150 milliliters of acid solution, concentration 0.5%, 1.0%, 2.0% or 5.0%, on short pieces of glass rod lying on the bottom of a 400 milliliter beaker. The pieces of glass rod assured that any corrosion would take place on all six surfaces, though we were mainly interested in the action on the trowelled surface. The cubes were exposed for 1 day, then 4 days more, then 10 days more; the spent acid was replaced with a fresh supply at the 1, 5, 8, and 12 day intervals. At the end of 1 day, 5 days, and 15 days, the cube was scrubbed and rinsed after being washed in running water, dried with a towel and in air for 15 minutes, and weighed. After the 1 and 5 day weighings, the cube was then replaced in the beaker with fresh acid.

Toward the latter part of our year, it was decided, because of the limited amount of time remaining and the large number of samples to be tested, to eliminate the 0.5% and 1.0% concentrations from the tests. This had very little effect on an overall interpretation of the year's work, however, because the 2.0% and 5.0% concentrations alone gave sufficient data for comparison. All four acids, however,-- Hydrochloric, Acetic, Lactic, and Phosphoric--, were used throughout the year.

Continuous Flow Acid Tests

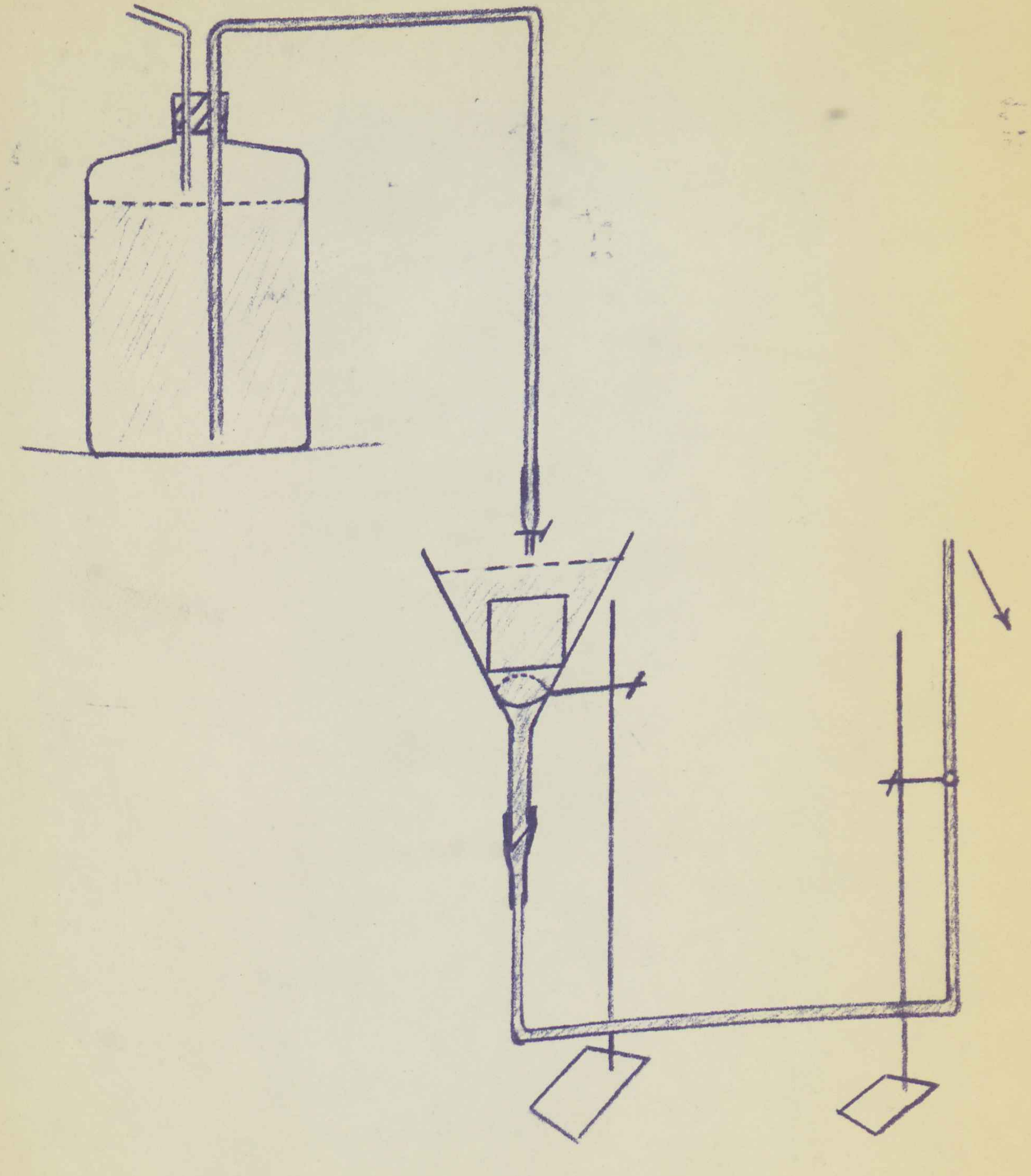
A new type of experiment that we devised during the year we called our Continuous Flow Acid Test. In addition to running the normal acid tests on cubes of varying composition, where we wished to determine under actual conditions, what would happen if acid was accidentally spilled on a concrete floor made with cement containing these various additives, or was used in cleaning the floor, and accidentally was not completely removed or washed away, we also wanted to ascertain what would happen if a steady stream of acid, almost unvarying in concentration, flowed on or over a concrete floor, or was channeled through some sort of concrete container. In order to do this, we set up special apparatus (Figure 4). Mounting the 2"x2"x2" cube in a large glass funnel with acid solution completely covering it, we maintained the acid level by a constant level overflow. With fresh acid solution dropping steadily at a constant rate from a large supply into the liquid above the surface of the cube, partially spent solution flowed out by means of the overflow, after having passed down over the entire surface of the block and into the lower end of the funnel. Two different acids were used, both 0.5% concentration, and the results are noted later under Experimental Results.

The Heating of Concrete Cubes

Since we were interested in resins, most of which would "set" with heat addition, we decided to see what effect high temperature heating would have on concrete blocks, and if no noticeable or measurable harm was apparent at moderate temperatures, to attempt the heat conversion of the resin in cubes containing Melmac 480, the melamine formaldehyde resin mentioned previously, and then to test these "converted" cubes for acid corrosion resistance. The resin in its converted form, alone, was supposedly highly acid resisting, according to the

FIGURE 4

CONTINUOUS FLOW APPARATUS



company specifications. It was therefore felt that if the resin could be converted in the concrete block, it could improve quite well the resistance to corrosion of the concrete by acids. Subsequently, we ascertained that heating of the concrete up to the temperatures which were necessary for the conversion of most resins (less than 200 degrees Centigrade) would not harm the concrete if the lost water was replaced by allowing the cube to remain in water overnight. We therefore carried out corrosion tests with the cubes containing Melmac 480 which had been heated in an oven at 200 degrees Centigrade for two hours in an attempt to convert the resin.

We made special effort to secure samples of resinous materials which required very little or no heat at all for "set", but which would set with time and/or in an alkaline medium such as cement. One of those which we were successful in getting was a phenolic resin (Schenectady Varnish Company Phenolic # SP 8023). This resin sets with time in an alkaline medium, or more rapidly if heated to moderate temperatures (around 100 degrees Centigrade). A series of cubes, made in Catskill, containing 1% of this resin, was heated at 105 degrees Centigrade for 1½ hours, cured in water, and sent to us for quantitative acid tests.

The results of the tests on both of these cube sets are presented under Experimental Results.

The Study of Plastics and Resinous Materials

In undertaking the study of these materials, we sought some additive suitable for incorporation into cement, sand and water mixtures which would impart special desirable properties to the hardened concrete. These desirable properties, of course, are numerous and include, among others, an increase in strength, an increase in resistance to corrosive action of water, acids and other chemicals, and a decrease in density and resulting increase in air content consistent with strength. Certain necessary conditions for this resinous additive, however, must also be taken into account. For example, the additive must not accelerate or retard too greatly the time of set of the concrete, nor can it hinder a firm set; the additive and the cement, sand, water mix must be mutually compatible and innocuous; the additive must be able to "set" at reasonable temperatures in an alkaline medium and must not alter any desirable properties of ordinary concrete; the additive must not be prohibitively costly.

With these requirements in mind, we surveyed the vast literature of plastics and resins-- primarily in order to learn about composition, nature and properties, but also to get some clue or idea as to their relative worth in our work with cement.

There are, in general, four classifications of resins. They are: Synthetic Resins, Cellulose Derivatives, Protein Plastics, and Natural Resins.

The Natural Resins include such things as shellac, rosin, rubber, asphalt and pitch. Protein Plastics include casein and soybean meal types using formaldehyde as a hardening agent.

The cellulose derivatives include cellulose nitrate and cellulose acetate polymers. The Synthetic Resin is the largest and most rapidly expanding type, and it is this type which we worked with most during the year; the classification includes the phenolics, ureas, melamines, alkyds, silicones, and many others.

Our plan of action in attacking this enormous field was eightfold:

1. Testing the basic ingredients or components of all the different kinds of Synthetic Resins and of some of the other types of resin also, alone and in the combinations which form the various resins, in order to determine compatibility with cement, sand, water mixtures.

2. Ascertaining which, among all of these resins, offered, on the basis of property study, the best chance for achievement of our goal-- improvement of chemical and physical properties of concrete.

3. Tabulating those types which specifically appeared favorable on the basis of the first two steps above, together with trade names and the manufacturers from whom they could be obtained.

4. Securing several samples of each of the favorable types.

5. Conducting preliminary tests in Schenectady to determine the advisability of submitting the material to Catskill for experimentation there.

6. Molding of 2"x2"x2" cubes containing these

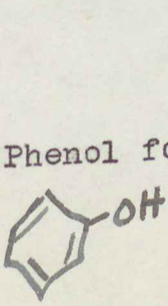
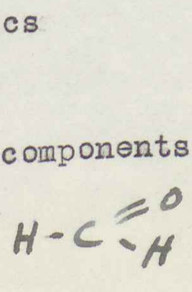
materials at Catskill so that compressive strength tests could be made on them in Catskill and acid tests on them in Schenectady.

7. Running of acid tests on the cubes.

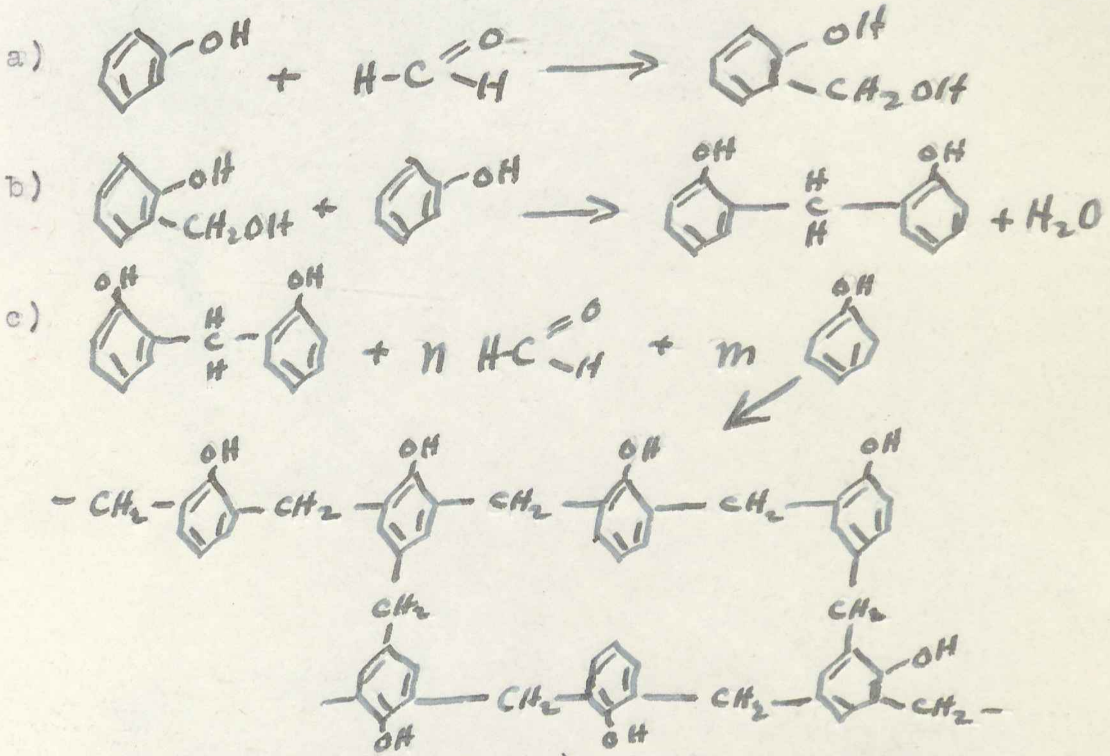
8. Evaluating the laboratory results in relation to the purpose of the study.

In order to test the various basic components of the resins, it was first necessary to identify them. The important plastics were sought out and listed with their component parts where this information was available. The first three in the list below are called <u>thermosetting</u> resins-- those resins which harden or cure with the application of heat but which, after curing has taken place, will no longer soften or "flow" when heated. Mason and Manning (15) give as the reason for this phenomenon: "certain chemical changes (caused by heat)...... result in the formation of a compact, cross linked, interdependent system". The others in the list, with the exceptions noted, are all <u>thermoplastic</u> resins-- those resins which exhibit the property of softening with heat, because the lack of free functional groups in this type of linear polymer prohibit further chemical reaction with the addition of heat, and causes them to remain permanently plastic, as a result.

The Important Plastics

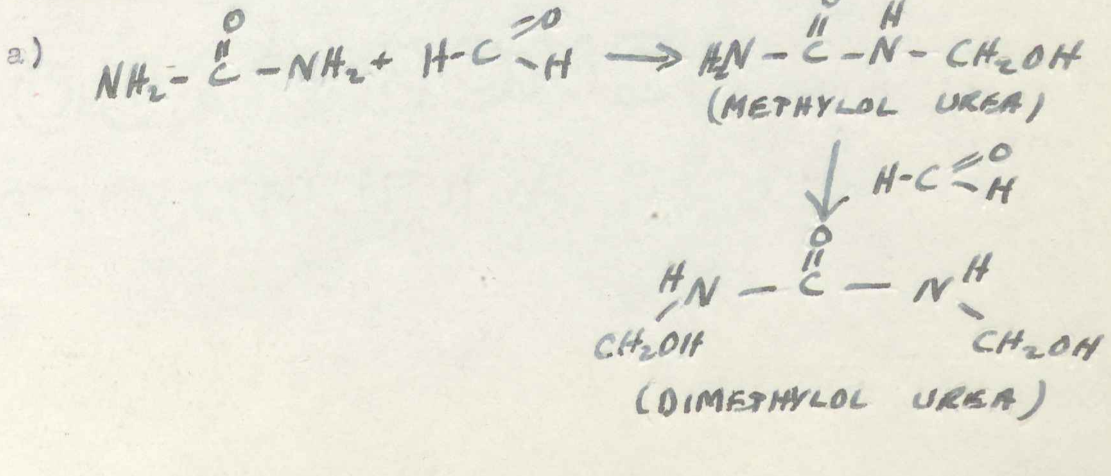
1. Phenol formaldehydes-- basic components: phenol,  and formaldehyde,  $H-C\begin{matrix}=O\\-H\end{matrix}$.

Simonds (16) relates that a great variety of phenolics are obtainable by a simple variation in ratio of phenol to formaldehyde, and by using different catalysts for set. Basically, however, the polymerization can best be described by the following reactions:

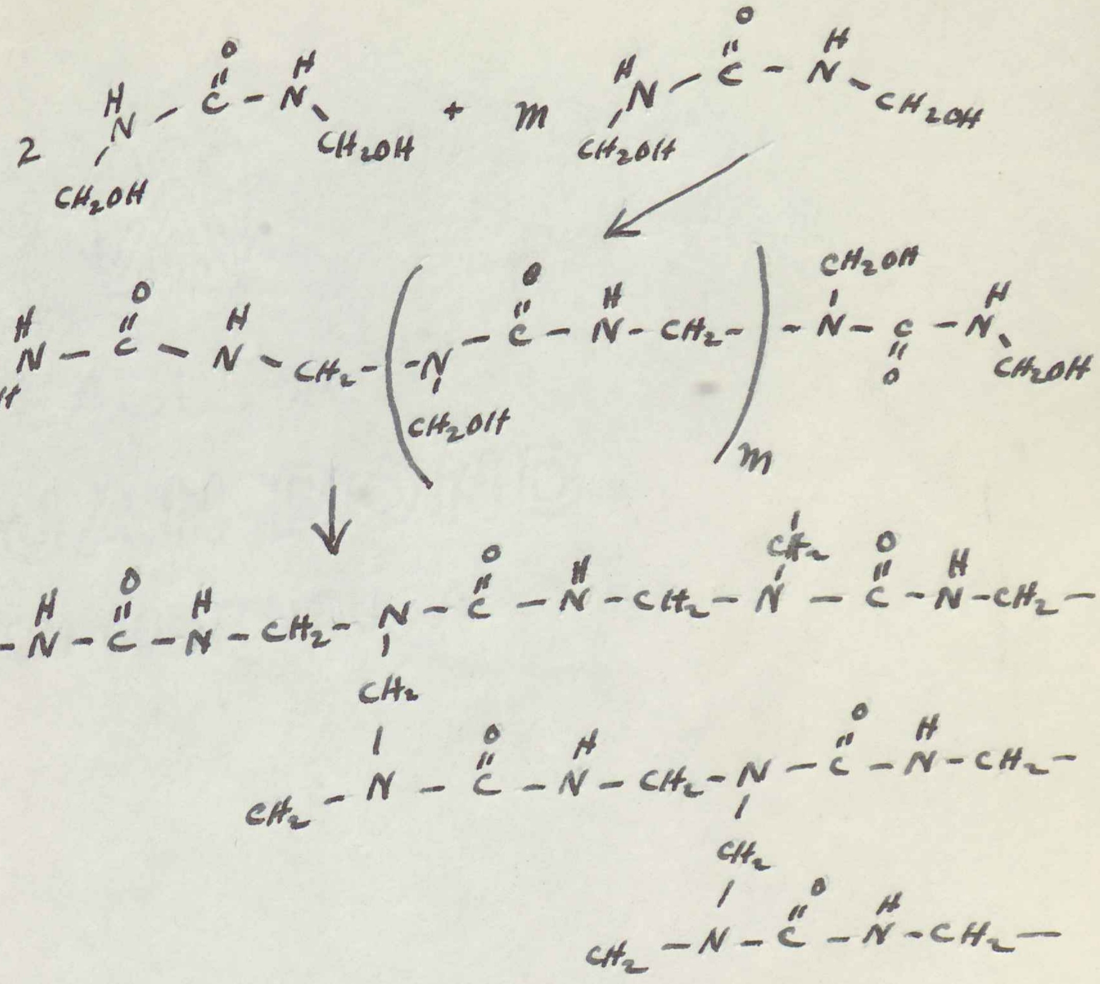


2. Urea formaldehydes (aminoplasts)-- basic components: urea, $NH_2-\overset{O}{\overset{\|}{C}}-NH_2$ and formaldehyde, $H-C\genfrac{}{}{0pt}{}{=O}{-H}$.

Though the mechanism of the reaction is not certain, the following steps are probable:

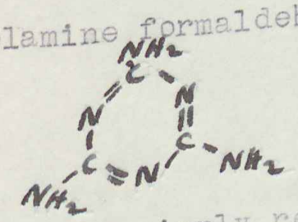


b)

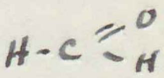


3. Melamine formaldehydes-- basic components:

melamine,

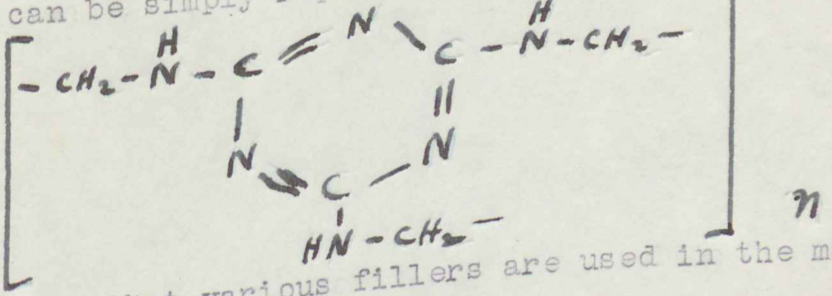


and formaldehyde,

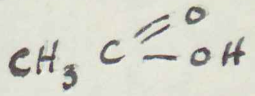


$H-C\overset{O}{\underset{H}{<}}$.

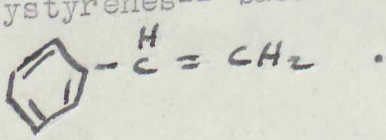
The polymer can be simply represented by the formula:



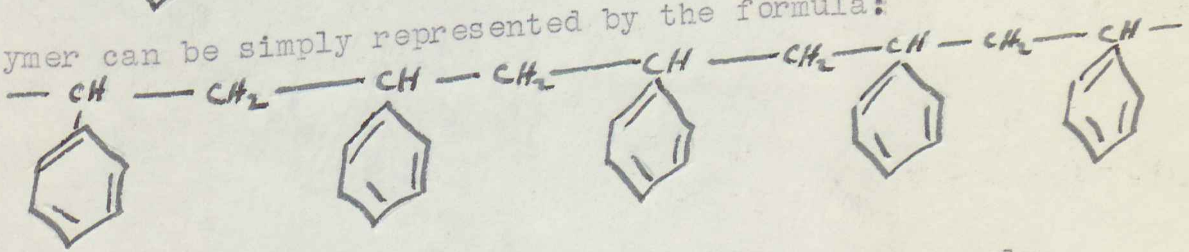
It is noted here that various fillers are used in the manufacture of this product, to impart certain desirable properties to it; e.g., cotton or rag fillers for resistance to impact, or mineral fillers for resistance to heat.

4. Cellulose acetates and Cellulose nitrates-- basic components: cellulose and acetic acid,  $CH_3C\overset{O}{=}{-}OH$ or nitric acid HNO_3.

The acidic nature and properties of the cellulose resins indicated that they would be of little value to us.

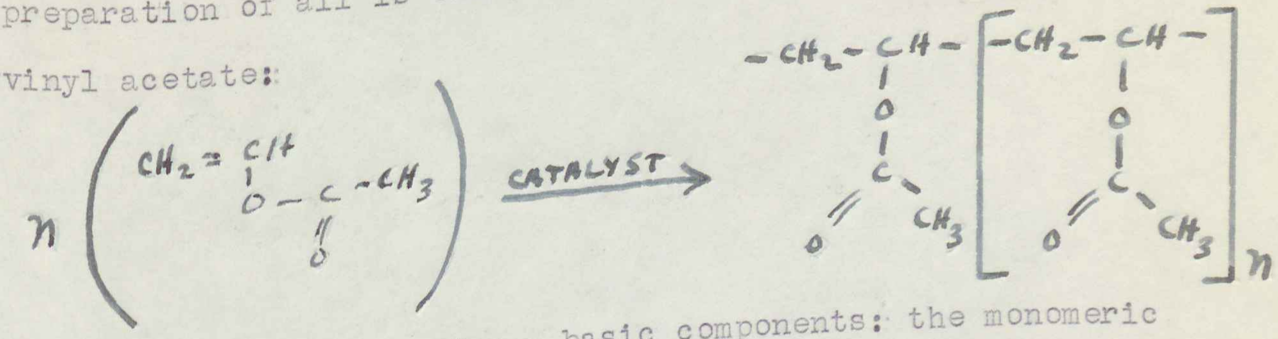
5. Polystyrenes-- basic components: styrene,  .

The polymer can be simply represented by the formula:



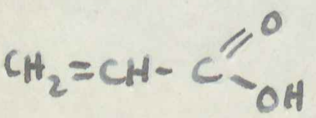
6. Vinyl copolymers (including polyvinyl acetate, polyvinyl chloride, polyvinyl chloride-acetate copolymer, polyvinyl alcohol, polyvinyl acetals, polyvinylidene chloride)-- basic components are the monomers.

The preparation of all is exemplified by the preparation of polyvinyl acetate:

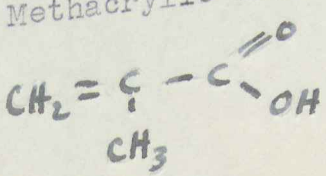


7. Methyl Methacrylates-- basic components: the monomeric derivatives of acrylic and methacrylic acid (commercially, the esters are important):

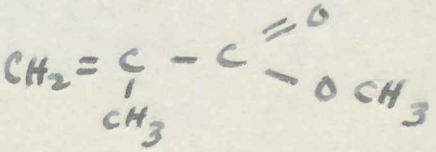
Acrylic acid



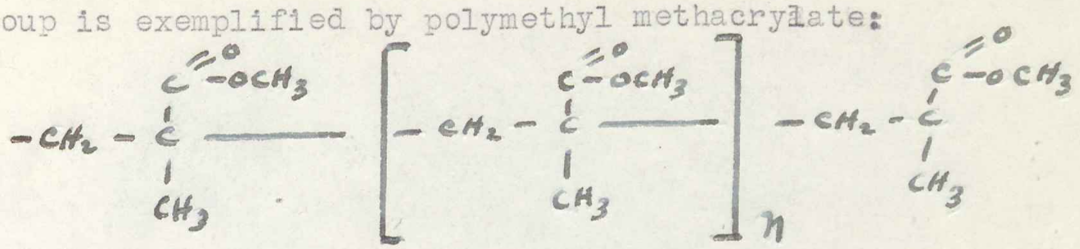
Methacrylic acid



Methyl methacrylate ester



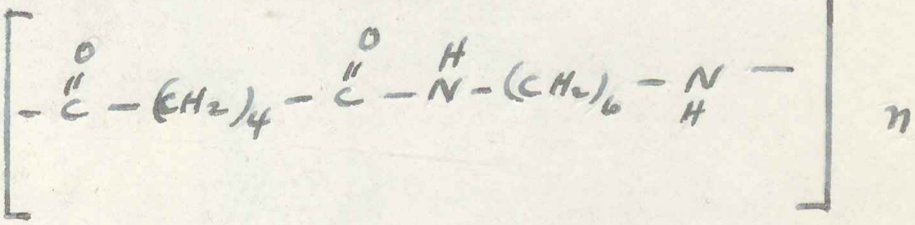
The group is exemplified by polymethyl methacrylate:



$$-CH_2-\underset{CH_3}{\overset{C(=O)-OCH_3}{C}}-\left[-CH_2-\underset{CH_3}{\overset{C(=O)-OCH_3}{C}}-\right]_n-CH_2-\underset{CH_3}{\overset{C(=O)-OCH_3}{C}}$$

8. Polymides (Nylon)-- basic components: diamines, dibasic acids or amide forming derivatives.

The formula for the polymer (Nylon):

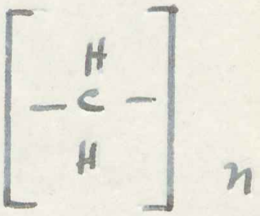


$$\left[-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-(CH_2)_6-\underset{H}{N}-\right]_n$$

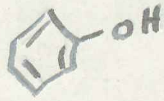
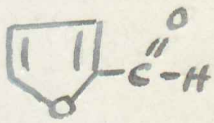
9. Polyethylenes-- basic component:

ethylene, $CH_2 = CH_2$.

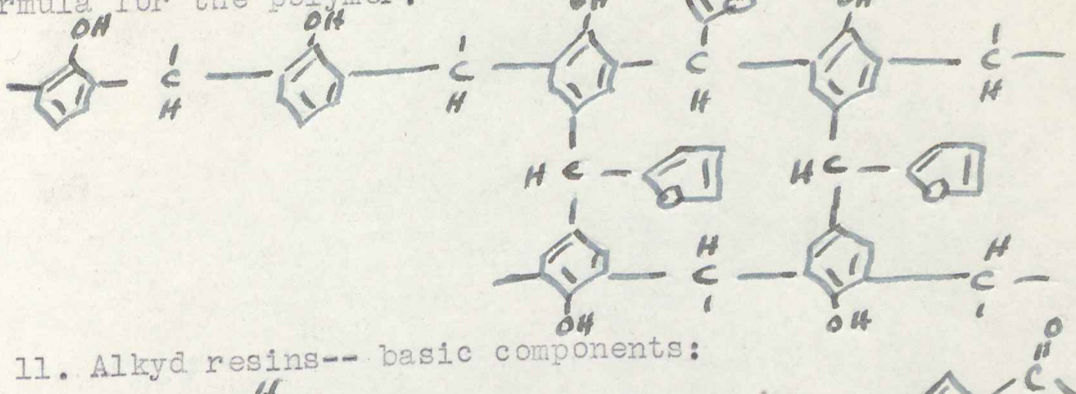
The formula for the polymer:



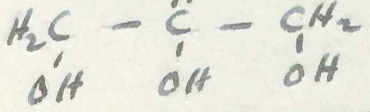
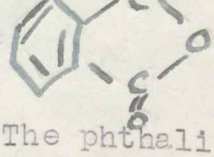
$$\left[-\underset{H}{\overset{H}{C}}-\right]_n$$

10. Phenol furfural (a thermosetting resin)-- basic components: phenol,  and furfural, .

The formula for the polymer:



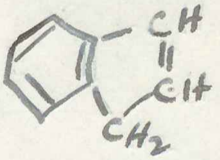
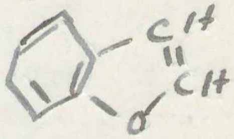
11. Alkyd resins-- basic components:

glycerol,  and phthalic anhydride .

$$\underset{OH}{H_2C}-\underset{OH}{\overset{H}{C}}-\underset{OH}{CH_2}$$

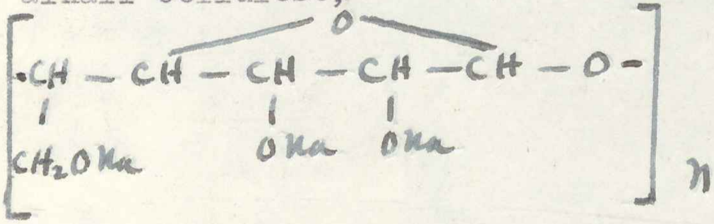
These resins are sticky, gummy, and slow in setting. The phthalic anhydride is insoluble in water. This type, therefore, was of very little use in our work.

12. Indene plastics-- basic components:

indene,  and cumarone,  .

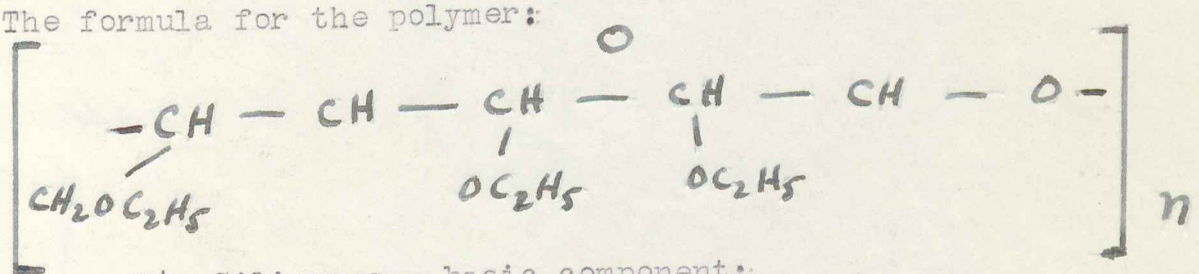
13. Ethyl cellulose-- basic components:

alkali cellulose, and ethyl chloride,



CH_3CH_2Cl

The formula for the polymer:

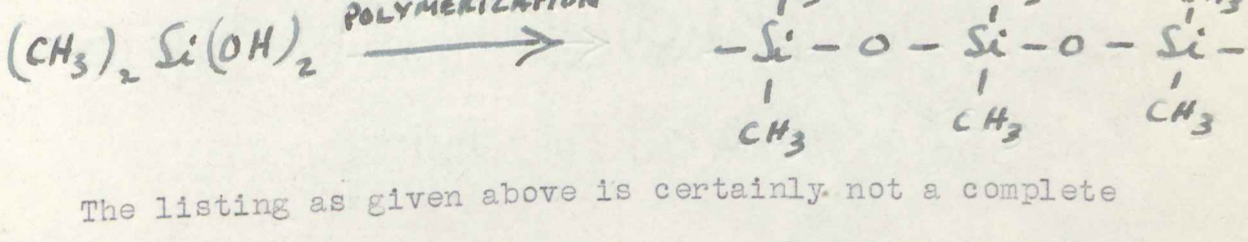


14. Silicones-- basic component:

silicon tetrachloride, $SiCl_4$.

The following reaction is typical of the preparation of the silicone resins:

$$SiCl_4 + 2\underset{\text{GRIGNARD REAGENT}}{CH_3MgX} \longrightarrow (CH_3)_2SiCl_2 \xrightarrow{2H_2O} 2HCl + (CH_3)_2Si(OH)_2$$



The listing as given above is certainly not a complete one, for we have purposely omitted the somewhat less important and less promising resins such as the allyls, the thioureas, the caseins, rubber and rubber-like materials, the lignin and soybean plastics, etc. In working with these components, we have tried to be as selective as possible without eliminating any possibility which showed the slightest promise.

While the above list of components and others not mentioned above were being tested in our laboratory, the literature was continually being searched to find out whether the properties of the plastic alone would be advantageously usable in our work. Of much help in narrowing down the possibilities was the Plastics Properties Chart of the Modern Plastics Encyclopedia Issue (13). From a study of this chart and of the reference text by Richardson and Wilson (17), and with our laboratory tests on components in mind, we prepared a list of what we believed to be the most promising prospects. We sought the following properties in the resins: high compressive, flexural, and tensile strength; high resistance to impact; high resistance to heat; varied color possibilities; a negative sunlight effect; and high resistance to corrosion by weak and strong acids and alkalies. The list (Table 1) denotes the resin type, and the trade names under which these are available. In most cases, more than one trade name is given for each type of resin because of the large number of variations possible within each type. The numbers following the trade names refer to the manufacturers, listed in Table 2.

Unfortunately, we were not successful in securing all of those in the list because of the limited time we had, and the rather lengthy delay on the part of the manufacturers in answering our requests and necessarily discreet inquiries.

During the course of the year, however, we managed to

TABLE 1. RESIN TYPES AND TRADE NAMES

TYPE	TRADE NAMES
Melamine formaldehyde or melamine-urea formaldehyde (Melurac)	Fiberite (1), Melantine (2), Melmac (3), Melurac (3), Plaskon (4), Resimene (5).
Phenol formaldehyde or phenol furfural (Durite)	Resinox (5), Durez (6), Durite (7), Bakelite (8), Heresite (9), Plenco (10), Textolite (11).
Silicone	Bakelite (8), GE Silicone (11), Dow Silicone (12).
Epoxy	Araldite (2), Pylene (13), Cardolite (14).
Polysulfide epoxy	Polykast (13), Thiokol (15).
Polystyrene or polystyrene butadiene (Pliolite)	Lustrex (5), Bakelite (8), Styron (12), Pliolite (23).
Vinylidene chloride	Saran (12)
Polytetrafluoroethylene	Teflon (16), Chemelec 300 (17), Fluoroflex-T (18).
Acrylate and Methacrylate	Plexiglas (19), Lucite (16).
Polymide	Nylon (16), Nylatron (20), Gering NRW (21).
Polyvinyl chloride plasticized	Marvinol (22), Pliovic (23), Geon (25).
Chlorinated rubber	Parlon (24).
Latex	Lustrex (5), DuPont Latex (16)

TABLE 2. RESIN MANUFACTURERS

Number	MANUFACTURER	ADDRESS
(1)	The Fiberite Corporation	Winona, Minnesota
(2)	Ciba Company, Inc.	New York, New York
(3)	American Cyanamid Co.	"
(4)	Barrett Div., Allied Chemical and Dye Corporation	"
(5)	Monsanto Chemical Company	Springfield, Mass.
(6)	Durez Plastics and Chemicals	North Tonawanda, N.Y.
(7)	The Borden Company	New York, New York
(8)	The Bakelite Company	"
(9)	Heresite and Chemical Co.	Manitowoc, Wisconsin
(10)	Plastics Engineering Co.	Sheboygan, Wisconsin
(11)	General Electric Co.	Pittsfield, Mass.
(12)	Dow Chemical Co.	Midland, Michigan
(13)	Polymer Industries Inc.	Springdale, Conn.
(14)	Irvington Varnish and Insulator Div., Minnesota Mining and Manufacturing Co.	Irvington, New Jersey
(15)	Thiokol Corporation	Trenton, New Jersey
(16)	E.I.DuPont de Nemours Co.,Inc.	Wilmington, Delaware
(17)	United States Gasket Co.	Camden, New Jersey
(18)	Resistoflex Corporation	Belleville, N.J.
(19)	Rohm and Haas Co.	Philadelphia, Pa.
(20)	The Polymer Corporation	Reading, Pa.
(21)	Gering Products Inc.	Kenilworth, N.J.
(22)	Naugatuck Chemical Co.	Naugatuck, Conn.
(23)	Goodyear Tire and Rubber Co.	Akron, Ohio
(24)	Hercules Powder Co., Inc.	Wilmington, Delaware
(25)	B.F. Goodrich Chemical Co.	Cleveland, Ohio

study rather completely eight different types of resins, and including several diversifications of what were two of the most promising types: the melamines and the phenolics. The eight types were:

a) phenol formaldehyde (3 variations)
b) phenol furfural
c) resorcinol formaldehyde
d) urea formaldehyde
e) melamine formaldehyde (3 variations)
f) polyvinyl chloride vinylidene chloride copolymer
g) latex
h) silicone

We also received another latex product very late in the year, but no experimental work was done on it.

The Laboratory Work

The laboratory work on these resins consisted of three steps: step 1, qualitative and semi quantitative testing of the basic components of resins; step 2, a qualitative and semi quantitative testing and evaluation of the promising resins; step 3, quantitative acid corrosion testing in Schenectady of concrete cubes made, in most cases, at Catskill, with these materials incorporated into the mix. In steps 1 and 2, we noted especially any development of unusual properties with Portland cement and the additive. This, of course, was done in order to catch any tendency on the part of the mix, toward simulation of the properties of Blue Bond mortar cement.

Step 1 was carried out as follows: 100 grams of Portland cement and 25 milliliters of water were used as the "standard" mix, the consistency being judged only qualitatively. No sand was added. The various resin components, with certain additions to and omissions from the list presented previously (based on their availability), were added to a mix of 100 grams of Portland cement and enough water (about 25 milliliters) to achieve a "normal" consistency. These materials were added separately, in percentages ranging usually from 1% to 10% by weight of the cement; then, suitable combinations of components were tried in the mix, again in varying percentages. The combinations, e.g., phenol and formaldehyde, probably did not form any polymers when combined this way, nor did we expect such to happen.

In each case, the solution (water plus additive or additives) was poured into the void surrounded by the curcular wall of cement (much as the mason mixes his concrete). The liquid was then covered with cement from the outer portion to prevent evaporation, and after allowing time for the cement grains to soak up most of the liquid, the mix was thoroughly blended using a trowel, formed into a ball, worked with the trowel again, and finally deposited in a paper lined cup cake mold, where it was allowed to set. The mixing process was carried out entirely on a steel plate. In these tests, we attempted to determine several things: the ease of mixing and compatibility of the additive with the cement and water; any precipitation caused by the additive; any significant volume or density difference as compared to the "standard" (seeking air entrainment); comparative time of set (semi quantitative only, Vicat test not used); physical propertiesof the mix (butteriness or "fat", workability, color changes, etc.). A summary of the results on step 1 is presented later in the section of Experimental Results.

Step 2 laboratory work followed the following outline:

a. Qualitative physical analysis of the resin, including company specifications on their product.

b. Measurement of pH if liquid; test for solubility in water.

c. Tests on the resin alone

1) Ordinarily, what are the conditions for set of the material?

2) After set, does it exhibit unusual properties of acid or water resistance?

3) How does a high alkalinity affect the setting process, if at all?

d. Tests with the resin in a cement and water mix

1) Compatibility and ease of incorporation into mix was determined.

2) Do desirable properties of butteriness, etc., develop in any of these mixes?

3) How is the cement set time affected by the resin addition?

4) How do the physical properties of these mixes with the resins differ from untreated cement-water mix after set?

5) Qualitative water and acid resistance tests on the cakes after set.

e. Evaluation of the additive.

The cakes for part "d" of step 2 were made in the same way as were those for step 1. The results for step 2 are also presented under Experimental Results.

Step 3 followed if the evaluation of the resin in step 2 was at all favorable. At Catskill, the maximum amount of each of the materials we submitted to them was incorporated into a series of 2"x2"x2" cubes made with floor topping mixes of concrete by intergrinding the material, in most cases, with the cement. Some additions were made to the mixing water also, but the main effort focused on intergrinding, since the corporation's interest tended toward successful intergrinding of a promising material with the product to be marketed. The cubes made at Catskill were sent to us in Schenectady, and we carried out step 3, the quantitative acid corrosion tests, in the manner described previously under Acid Tests (Page 19). The results of these tests are presented in the next section, Experimental Results.

EXPERIMENTAL RESULTS

For the sake of simplicity, this section will be divided into eight parts; Part 1 will contain results of step 1 of the laboratory work consisting of the qualitative and semi-quantitative testing of the basic components of resins; Part 2 will contain results of step 2 of the laboratory work consisting of the qualitative and semi-quantitative tests on the resins themselves; Part 3 will contain the results of strength tests made at Catskill on concrete blocks containing the various additives; Part 4 contains the results of acid tests, run partially on the old basis, on concrete cubes of Anti-Bacterial Cement and of the floor topping basis for ABC, Blue Streak Air Entraining cement; Part 5 is the tabulation of changes in pH during acid tests; Part 6 consists of results of the acid tests, run with the modified procedure as explained previously, on concrete cubes containing the various resins with which we worked this year; Part 7 describes results on the Continuous Flow Acid Tests; Part 8 is concerned with acid tests on 2 sets of cubes, 1 containing Melmac 480, the other containing a phenolic resin, both sets having been heated in order to try to convert the resin to its permanent form. These acid tests are compared with tests on unconverted cubes containing the same additives.

Part I

Except where modification is indicated, all of the ingredients tested were added in percentages of 0.5, 1.0, 2.0, 5.0 and 10.0 per cent each, and the results on each studied.

Formaldehyde additions mixed easily in all percentages, formed no precipitates, and developed no desirable properties of butteriness, etc. No distinct volume increase due to air entrainment was noted when compared with the"standard". As the percentage of formaldehyde added was increased, the time of set decreased; the strength of the set cakes appeared unharmed due to the formaldehyde.

Phenol additions mixed easily; no precipitates or butteriness was noted, nor was there any distinct volume increase. The time of set was slightly less than normal and unvarying as the phenol percentage was increased. A pink color, characteristic of phenol, cement and water mixes, appeared in samples containing the higher percentages of additive. Less water was required for a normal mix as the phenol percentage rose; the strength of samples with less than 5% phenol appeared normal, and those with 5% and 10% phenol were only slightly weaker than normal.

Phenol and formaldehyde together mixed well with the cement in the percentages under 5%. The time of set decreased slightly with increasing percentages; no precipitates were formed; there was no simulation of BB mortar cement.

Urea was compatible; it mixed well, formed no precipitates, and did not simulate BB cement. Times of set were normal; however, the 5% and 10% samples did not set well and were weak.

Urea and formaldehyde mixed well; set time was accelerated in each case, and no BB simulation was apparent. The higher percentages did not set well and were weak.

Glycerol and glycol (separately) mixed well in all cases. Set times in both kinds of mixtures were accelerated. No simulation of BB cement took place, no predipitates were noted, and the strength was unaffected by increased additive concentrations.

Phthalic anhydride could not be incorporated into a cement-water mix; therefore, combinations with glycerol and glycol, with which it forms alkyd resins, were also impossible in our tests.

Cresol addition caused a loss of cohesiveness in the mix. No desirable properties simulating BB cement were in evidence; set times appeared normal and no precipitates were formed.

Casein was water insoluble, and could not be used in this work.

Vinyl acetate was tried also, but appeared to offer no advantages with its use.

Many of the other ingredients were unavailable in our laboratory, and therefore could not be tested.

Summary: The addition of these resin components, alone and in combination appears to do no harm to the cement-water mix at concentrations not exceeding 2.0% by weight of the cement. No desirable properties such as those exhibited by the Blue Bond mortar cement have developed as a result of these additions, however. One undesirable property may be the accelerated set time exhibited in some cases. This component test list was necessarily incomplete.

Part 2

Phenol formaldehyde--3 variations studied. The *first variation*, a liquid phenolic (Schenectady Varnish Company #SP 609) proved entirely incompatible with a cement and water mix as it destroyed the strength of the resulting "concrete" completely. The *second variation*, another liquid phenolic, (Schenectady Varnish Company #SP 8023) appeared to be water soluble and compatible in all proportions with the cement and water mixes. Though no simulatiion of mortar properties was discovered here, the resin appeared to impart some added protection to the concrete surface against water and acid action. Heat conversion was tried with this resin also, and favorable results were obtained upon immersion of the concrete in acid solution. This resin was a water soluble, heat reactive phenolic which would polymerize at room temperature in an alkaline medium with time. Its specific gravity upon receipt in our laboratory was recorded at 1.22. the resin was sent on to Catskill for further testing and cube making. The *third variation* was Monsanto Chemical Co.'s liquid bonding resin, "Resinox 468". It was a clear, tan colored liquid with a pH value of 7.2. Its solubility in water is an inverse function of time: the longer it stands, the less soluble it is. A temperature exceeding 100 degrees Centigrade polymerized the material alone. It was compatible with the cement and water, but not in all proportions, a whitish precipitate forming in water solution when the solubility limit was reached. Set times were greatly retarded;

other physical properties of the mix remained "normal". The addition of this material produced no unusual acid corrosion resistance. A sample was forwarded to Catskill for further testing and cube making since no undesirable properties, outside of set time retardation, appeared.

Phenol furfural-- 1 sample studied: The Borden Company's "Durite S4120", a phenol furfural novolak converted by 10% hexamethylene diamine to a thermosetting plastic. It was a brown solid in various size chunks, the smaller pieces resembling iodine crystals in luster and color. A phenol odor was present. This material was insoluble in water and was converted to the polymer at a temperature greater than 125 degrees Centigrade. The resin appeared to be water and acid resisting, and was difficultly mixed with cement and water, though it appeared to be compatible. A normal setting time was noted and a lighter weight, darker colored cake resulted with no outstanding acid resistance noted. The sample was sent to Catskill.

Resorcinol formaldehyde-- 1 sample studied: Schenectady Varnish Company's Resorcinol # 1505-A. A viscous, reddish brown liquid of pH originally 2.0 but raised to 9.0 by the addition of NaOH. A high alkalinity appeared to enhance the set ot the material. It appeared to be water and acid resisting; the unpolymerized material was compatible when mixed with cement and water. No simulation of mortar cement properties occurred; the set time was accelerated appreciably. The sample was sent to Catskill.

Urea formaldehyde-- 1 sample studied: Dimethylol urea. We found that this material offered no particular advantage when used with cement in our work. It was tested early in the year, and found to be insoluble in water and incapable of being distributed homogeneously in a cement-water mix. It had only poor resistance to acid corrosion, and was therefore discarded as a possibility. No cubes were made containing this resin, though the compressive strength of concrete with it as an additive was determined at Catskill.

Polyvinyl chloride-vinylidene chloride copolymer-- 1 sample studied: B.F.Goodrich Company's "Geon". This was a yellowish white solid, having no odor and being insoluble in water. Heating above 100 degrees Centigrade converts it into an acid resisting mass. This material was incorporated into our cement-water mix only with much difficulty, because of its water insolubility. The set time appeared to be retarded and no outstanding properties developed. The sample was forwarded to Catskill.

Melamine formaldehyde-- 3 variations studied. The first variation was American Cyanamid Company's Melmac 480, used by Dunbar (8) and in our work this year. It is a water soluble liquid only with the addition of alkali to the mixing water. This material was tested early in the year, and cubes of Portland cement containing it were made in our lab in Schenectady. It was compatible, but did not offer outstanding properties of acid corrosion resistance. The second variation was American Cyanamid Company's Melamine 421, and this was an unfilled melamine formaldehyde, free flowing, dry white powder. It was a water soluble low reacted form of a heat setting resin. Heating at a temperature above 150 degrees Centigrade converted this material to a plastic which appeared to be soluble in Hydrochloric acid and in water. It was discovered that, like Melmac 480, excess alkali was necessary for a uniform water solution. The set time of this cement-water-resin mix was close to normal, and no simulation of BB cement properties took place. This material was forwarded to Catskill for strength tests and cube making for our acid tests. The <u>third variation</u> was Monsanto Chemical Company's "Resimene 814", a melamine formaldehyde powder, water soluble, offering surface hardness, heat, abrasion, alkali and chemical resistance, according to the specifications sent to us. A white solid mass was produced with heat, stable to water and to acid to a reasonable extent. Alkali solution appeared to prevent the proper polymerization of the material. The normal polymerization was catalyzed to a few minutes time by the addition of the catalyst supplied by Monsanto-- Resimene RA-032, a liquid with pH equal to 7.6. In cement-water-resin mixes, no simulation of BB mortar properties was noted; a normal set time was observed, and there were signs of greater than usual resistance to corrosion, but no exceptional evidence. This material was also sent to Catskill.

<u>Latex</u>-- 1 sample studied; though another sample was received in our lab from the DuPont Company, no work could be done on it in connection with our project since it arrived extremely late in the year. The sample that was studied was Monsanto Chemical Company's Lustrex Latex 201, a white liquid of pH equal to 10.3 (this high pH was to be expected, since the latex is suspended in a solution of ammonia). Temperatures above 80

degrees Centigrade polymerized the material. It was completely compatible in the cement-water mix, and developed no outstanding properties of the BB mortar cement. The set time of this cement-water-resin mix was greatly accelerated, to the extent of about ½ of the normal time required. Corrosion resistance was not exceptional, but deserved some note. The sample was forwarded to Catskill.

Silicone-- 1 sample studied: General Electric Company's Silicone # 81543 (developmental sample), a liquid, greenish yellow in color, with a density of 1.052 and a pH value of about 5.0. Heating at temperatures greater than 100 degrees Centigrade set a sample of this resin somewhat, but on the addition of alkali, a rapid set took place. The set resin was definitely water resisting and appeared to be acid resisting also. It was completely compatible in cement-water mixtures, and accelerated the set times of these mixes slightly above normal. Slight but not exceptional "butteriness" was observed in the mixes. No harm in strength of the resulting set cake was apparent. This sample was sent on to Catskill for further testing and for incorporation into cubes for quantitative acid tests.

Summary: Of the eight types of resins studied, only the urea formaldehyde sample (dimethylol urea), one variation of the phenol formaldehyde type (Schenectady Varnish Co. #SP 609), and one variation of the melamine formaldehyde type (Melamc 480) were not sent to Catskill for further testing and cube molding: the phenolic and the urea resins not sent were deemed not worthwhile in this work, and cubes containing Melmac 480 with Portland cement were cast in Schenectady using the gang mold fitted with tempered masonite squares as described previously. None of the other resins tested exhibited undesirable properties for the most part, and all were therefore forwarded to Catskill, where 2"x2"x2" cubes of a floor topping mix containing them as additives were cast.

Part 3. Compressive Strength Test Results

All compressive strength tests were carried out at Catskill on their compression testing machine. Tests were made this year on samples containing the following additives:

(1) Sodium Methyl Siliconate (General Electric Co.)

(2) Melmac 480 in percentages varying from 0.01% to 10.0% by weight of the cement.

(3) Anti-Bacterial Cement alone and in combination with Portland cement (50% each in the second instance).

(4) Dimethylol urea in percentages varying from 1.0% to 5.0%.

(5) Phenolic SP 8023

(6) Silicone 81543

(7) Melamine 421

(8) Durite S4120

(9) Resorcinol resin 1505-A

(10) Lustrex Latex 201

(11) Resinox 468

(12) Resimene 814 plus catalyst Resimene RA-032

(13) Geon

(14) Blank (standard, containing no additives).

For numbers (1) through (4) inclusive, curing in water for 28 days took place before testing. For numbers (9) through (14) above, one day tests were given. Unfortunately, we do not have the information on numbers (5) through (8), though we presume that the tests were made on these samples. The results of these tests appear in the data table on the next page; Table 3.

TABLE 3. COMPRESSIVE STRENGTH TEST RESULTS

SAMPLE CONTENTS	PER CENT ADDITIVE	COMPRESSIVE STRENGTH (PSI)
PC	0.0%	5130 (avg.)
PC and (1)	0.2	7135 (avg.)
PC and (2)	0.01	4792
"	0.05	4183
"	0.1	4458
"	0.5	3267
"	1.0	4250 (4300)
"	2.0	4375 (4825)
"	5.0	3400 (3675)
"	10.0	2750 (1750)
PC and (4)	1.0	5167
"	2.0	5125
"	5.0	5992
ABC	0.0	4425
ABC and (3)	50.0	4375
HES	0.0	2400
HES and (5)	0.1	
HES and (6)	0.1	
HES and (7)	0.2	
HES and (8)	0.1	
HES and (9)	0.1	2275
HES and (10)	0.1	2750
HES and (11)	0.1	2600
HES and (12)	0.1 & 0.25	2875
HES and (13)	0.1	2325

In the above table, PC stands for Portland Cement, ABC for Anti-Bacterial Cement, and HES for a floor topping mix of High Early Strength cement. The numbers in parenthesis refer to the list of additives on Pages 48 and 49.

The standard for comparison for all of the samples made with HES cement and compressive strength tested after curing in water after only one day was 2400 psi. We noted that none of the additives tested for which we have results, harmed the strength appreciably. In general, in most cases, the strength increased, though not greatly. It is seen that a 50% PC-50% ABC mix gives the same results (approximately 4400 psi) as a straight ABC mix, and both of these appear to have less strength than ordinary PC (5130 psi).

Increasing percentages of Melmac 480 appear to decrease the strength. The figures in parentheses alongside those for Melmac additives are the test results on samples which contained NaOH alone in the concrete in the same percentages used in the corresponding Melmac 480 sample. It is seen that there is little difference between the strengths of the two samples in each case, though the sample which contained the same quantity of NaOH as was used together with Melmac in the 10% sample, was tested much weaker (by 1000) than this 10% Melmac sample. This is perhaps explicable on the basis of the individuality of the samples, since they were poured at separate times from different batches. At any rate, it is certain that NaOH alone or with Melmac 480 in increasing percentages, decreases measurably, the strength of the concrete.

Dimethylol urea appears to have no effect on the strength, except that the 5% addition gave a sharp unexpected strength increase.

With the possible exception of the higher percentages of

Melmac 480 and NaOH, then, none of these additives appeared to harm the strength of concrete, based on a normal sample containing no additives; and in some cases, especially with the High Early Strength floor topping mixes, enhanced that strength slightly over the norm.

Part 4. Results of Unmodified Acid Tests on Concrete Blocks Made Up With Anti-Bacterial Cement and Blue Streak Air Entraining Cement..

There are results listed in Table 4 for two series of cubes tested using the 20 day duration and three acids, Hydrochloric, Acetic, and Lactic acids. The concentrations used are given also in the table. The BSAE cement we understand to be the basis for ABC cement.

The first column in the table lists the acid and its concentration; the second through fifth columns indicate the weight losses in percentage of original weight first of the ABC cube, then of the BSAE cube after 1 day of immersion, 3 days, 10 days, and finally after 20 days of immersion respectively.

TABLE 4. ACID TEST RESULTS ON ABC AND BSAE SAMPLES

PERCENTAGE LOSSES

ACID	1 Day Loss		3 Day Loss		10 Day Loss		20 Day Loss	
	ABC	BSAE	ABC	BSAE	ABC	BSAE	ABC	BSAE
0.35% H	.0	.0	.0	.0	.0	.0	.0	.0
0.70% H	.2	.3	.4	.5	.6	.8	.9	.9
1.00% A	.2	.2	.3	.2	.6	.3	.9	.5
2.00% A	.4	.2	.8	.7	1.0	1.0	2.0	1.3
1.00% L	.0	.0	.1	.0	.2	.2	.3	.2
2.00% L	.3	.0	.3	.3	.5	.5	.8	.7

H is Hydrochloric acid, A is Acetic acid, L is Lactic acid.

The ABC cubes were made using the following recipe: 666 grams of Anti-Bacterial Cement, 666 grams of concrete sand, and 1000 grams of stone, 3/8" to 8 mesh. The BSAE cubes used Blue Streak cement, concrete sand and stone in the same proportions.

As seen from the table, there is hardly any difference in corrosion on ABC and BSAE cubes except in the case of the Lactic acid, which seemed to corrode ABC slightly more than it did BSAE.

Part 5. Changes in pH During Acid Tests

A study of the effect of the concrete on the acids during acid tests was made in order to determine whether corrosive action on the concrete decreased the acid concentration seriously and whether, as a result, it was necessary to change the acid in the beakers more often during the course of the tests. Two different types of concrete cubes were used: one set contained Anti-Bacterial Cement, the other contained regular Portland cement.

The figures in Table 5 show what happens to the pH value of water or the acid solution (150 milliliters in each case) in the presence of 2"x2"x2" cubes of both ABC and regular Portland cement during four days of observation. Naturally, the same solution was used each time readings were taken, small samples having been removed for pH measurement with the Beckman pH meter.

TABLE 5. pH VALUES FOR SOLUTIONS IN CONTACT WITH CONCRETE CUBES.

	pH VALUES									
	START		1 DAY		2 DAY		3 DAY		4 DAY	
SOLUTION	ABC	PC	ABC	PC	ABC	PC	ABC	PC	ABC	PC
Water	6.0	6.0	11.5	11.6	11.5	11.7	11.5	11.9	11.6	12.0
0.5% H	1.0	1.0	5.3	4.9	7.6	5.1	9.4	7.7	11.0	8.7
1.0% H	0.7	0.7	3.3	3.0	4.6	3.4	6.2	4.1	9.0	4.7
2.0% H	0.4	0.4	2.9	2.0	3.6	2.9	4.5	3.3	5.1	3.7
5.0% H	0.1	0.1	2.7	0.6	3.4	1.2	3.8	2.0	4.2	2.6
0.5% A	3.3	3.3	5.2	5.0	6.2	5.8	10.5	10.0	11.1	11.2
1.0% A	2.9	2.9	5.1	5.1	5.7	6.0	7.7	9.1	10.7	10.7
2.0% A	2.7	2.7	4.7	5.0	5.3	5.2	5.8	5.7	6.4	6.3
5.0% A	2.4	2.4	4.7	4.5	5.1	4.5	5.3	4.9	5.3	5.4
0.5% L	2.5	2.5	5.0	4.6	8.3	5.1	11.1	11.0	11.4	11.8
1.0% L	2.3	2.3	4.3	4.4	4.7	4.6	6.1	6.0	10.7	11.7
2.0% L	2.2	2.2	4.1	3.8	4.6	4.1	5.6	5.0	6.7	5.6
5.0% L	1.8	1.8	4.0	2.5	4.7	3.8	5.5	4.3	5.7	4.5
0.5% P	1.7	1.7	4.2	4.7	4.9	4.8	5.0	4.9	5.4	5.3
1.0% P	1.5	1.5	3.3	3.1	4.2	3.5	4.4	4.3	4.3	4.5
2.0% P	1.3	1.3	2.7	2.6	3.2	2.9	3.8	3.5	4.1	4.3
5.0% P	1.0	1.0	2.4	2.2	3.0	2.4	3.4	2.8	3.5	3.1

H is Hydrochloric acid; A is Acetic acid;

L is Lactic acid; P is Phosphoric acid.

It is seen from this table that the acid weakens quite seriously during the attack on the cubes, with almost no difference in effect on solutions with either ABC or PC.

These results bear out what we had suspected; and on the basis of the results, suitable changes were made in the acid test procedure. These changes were indicated previously under Experimental Procedure.

Part 6. Acid Tests, Run with the Modified Procedure on Concrete Blocks Containing Resinous Materials as Additives.

Using the modified procedure outlined previoulsy under "Apparatus and Procedure", many acid corrosion tests were conducted on concrete cubes containing the resinous materials whose study has been described in Part 2 of this section.

There was an interesting result apparent when cubes of Anti-Bacterial Cement and cubes of regular Portland cement were acid corrosion tested and the resulting weight loss percentages compared as in Table 6.

TABLE 6. COMPARISON OF ACID TEST RESULTS ON ABC AND PC.

	PERCENTAGE LOSSES IN WEIGHT					
	1 DAY		5 DAYS		15 DAYS	
SOLUTION	ABC	PC	ABC	PC	ABC	PC
0.5% H	0.1	0.0	0.1	0.0	0.8	1.9
1.0% H	0.3	0.8	0.6	1.8	2.8	8.1
2.0% H	0.9	2.2	2.2	6.3	6.5	20.0
5.0% H	2.9	8.3	7.0	19.0	20.0	50.0
0.5% A	0.0	0.1	0.0	0.1	0.0	0.5
1.0% A	0.0	0.1	0.2	0.7	1.0	2.1
2.0% A	0.2	0.4	0.7	1.4	1.9	3.3
5.0% A	0.9	1.0	2.1	3.5	5.6	8.0
0.5% L	0.0	0.0	0.0	0.0	0.0	0.0
1.0% L	0.0	0.0	0.1	0.2	0.5	0.8
2.0% L	0.0	0.1	0.3	0.3	1.3	3.4
5.0% L	1.1	1.5	2.0	4.8	6.4	16.4
0.5% P	0.0	0.0	0.0	0.0	0.0	0.4
1.0% P	0.0	0.0	0.0	0.2	0.6	2.2
2.0% P	0.0	0.1	0.3	1.1	1.9	6.0
5.0% P	0.6	2.1	1.8	6.0	6.4	15.7

As expected, the data bear out our suspicion that the smoother cubes consisting of ABC cement would resist corrosion better than ordinary concrete cubes made with PC. Several conclusions can therefore be drawn from this data: Anti-Bacterial Cement is more acid corrosion resisting than regular Portland cement-- this is to be expected since the ABC cement is designed as a floor topping mixture; Hydrochloric acid gives the strongest attack in our tests, with Phosphoric acid next, followed by Lactic and finally Acetic acid; the amount of corrosion is in direct proportion to acid concentration and to time of exposure.

We next present two sets of results. The first set comprises tests on Portland cement cubes with no additives as compared to cubes made up with varying percentages of Melmac 480 in a PC, concrete sand (Ottawa graded) and water mix. The second set comprises tests on a High Early Strength concrete as standard compared with this same floor topping mix combined with 10 different resins. These results are tabulated as follows: first set, Tables 7a, 7b, and 7c; second set, Tables 8a, 8b, and 8c.

For the first set of data, Tables 7a, 7b, and 7c, certain abbreviations were used. These are given below with appropriate explanation:

1M is cube containing 1.0% Melmac 480 plus 0.25% NaOH (PC)
2M is cube containing 2.0% " " 0.35% " "
5M is cube containing 5.0% " " 0.70% " "
H is Hydrochloric acid, A is Acetic acid,
L is Lactic acid and P is Phosphoric acid.

TABLE 7a. ACID TEST RESULTS ON PORTLAND CEMENT CUBES CONTAINING MELMAC 480.

PERCENTAGE LOSS IN WEIGHT AFTER 1 DAY IMMERSION

SOLUTION	PC	1M	2M	5M
0.5% H	0.0	0.3	0.1	0.0
1.0% H	0.8	0.8	0.5	0.5
2.0% H	2.2	2.2	2.3	1.9
5.0% H	8.3	8.6	9.3	4.7
0.5% A	0.1	0.0	0.0	0.0
1.0% A	0.1	0.1	0.0	0.0
2.0% A	0.4	0.0	0.3	0.3
5.0% A	1.0	1.4	1.5	1.4
0.5% L	0.0	0.0	0.0	0.0
1.0% L	0.0	0.0	0.0	0.0
2.0% L	0.1	0.2	0.1	0.2
5.0% L	1.5	1.6	1.3	1.5
0.5% P	0.0	0.0	0.0	0.0
1.0% P	0.0	0.1	0.0	0.0
2.0% P	0.1	0.3	0.2	0.5
5.0% P	2.1	1.4	1.5	2.0

TABLE 7b. ACID TEST RESULTS ON PORTLAND CEMENT CUBES CONTAINING MELMAC 480.

PERCENTAGE LOSS IN WEIGHT AFTER 5 DAYS IMMERSION

SOLUTION	PC	1M	2M	5M
0.5% H	0.0	0.3	0.0	0.0
1.0% H	1.8	1.2	1.3	1.8
2.0% H	6.3	6.0	6.3	5.9
5.0% H	19.0	20.5	21.8	20.5
0.5% A	0.0	0.0	0.0	0.0
1.0% A	0.7	0.1	0.1	0.2
2.0% A	1.4	1.0	0.8	1.0
5.0% A	3.5	5.7	6.9	5.2
0.5% L	0.0	0.0	0.0	0.0
1.0% L	0.2	0.0	0.3	0.0
2.0% L	0.3	0.5	0.7	0.5
5.0% L	4.8	4.9	4.7	5.1
0.5% P	0.0	0.0	0.0	0.0
1.0% P	0.2	0.3	0.4	0.4
2.0% P	1.1	1.2	1.0	1.7
5.0% P	6.0	5.8	6.0	6.0

TABLE 7c. ACID TEST RESULTS ON PORTLAND CEMENT CUBES CONTAINING MELMAC 480.

PERCENTAGE LOSS IN WEIGHT AFTER 15 DAYS IMMERSION

SOLUTION	PC	1M	2M	5M
0.5% H	1.9	0.3	1.5	1.1
1.0% H	8.1	5.8	7.1	6.7
2.0% H	20.0	20.4	20.8	18.7
5.0% H	50.0	56.0	57.0	56.5
0.5% A	0.5	0.0	0.2	0.0
1.0% A	2.1	0.1	1.4	1.1
2.0% A	3.3	1.7	3.5	3.3
5.0% A	8.0	18.1	14.6	12.0
0.5% L	0.0	0.0	0.0	0.0
1.0% L	0.8	0.0	0.7	0.6
2.0% L	3.4	2.3	2.1	2.4
5.0% L	16.4	17.6	15.8	13.0
0.5% P	0.4	0.0	0.0	0.7
1.0% P	2.2	1.9	1.5	2.5
2.0% P	6.0	5.5	5.4	6.2
5.0% P	15.7	17.1	17.3	17.1

As one glances at the preceding tables horizontally across the page, a trend is noted. With Hydrochloric acid and Acetic acid, a slight decrease in corrosion is seen to take place as the percentage of Melmac 480 added is increased. There is almost a status quo with Lactic acid, and the corrosion caused by Phosphoric acid is seen to increase slightly with increasing percentage of this additive. The increased resistance to Hydrochloric acid and Acetic acid which seems to be present here is not great enough to warrant further research on the additive since these increases in corrosion resistance must be balanced against the decrease in strength, among other things, when weighing the value of an additive.

It is here noted that, since Sodium Hydroxide was needed to keep the resin in water solution, cubes of Portland cement containing the same amounts of NaOH as were used in the corresponding cubes with the resin (percentages were noted on Page 57) were also tested for their corrosion resistance, for the sake of comparison. The results were very similar to those already tabulated for the Melmac cubes, and are therefore not recorded here.

The additives in the tables on the next few pages are referred to by number for the sake of economy of space. The numbers refer to the listing which follows, in which all but additive #2 were interground with the cement. The #2 additive, which is the same as additive #1 (Phenolic SP 8023), was added to the mixing water rather than being interground with the High Early Strength cement used in making up the floor topping mix cubes that we have tested.

The additives below are referred to by their number in Tables 8a, 8b, and 8c.

ST is the standard, and contains no resinous additives.

1 contains 1.0% Phenolic resin, Schenectady Varnish Company #SP 8023.

2 contains 0.9% Phenolic resin, as above.

3 contains 0.1% Silicone resin, General Electric Company # 81543 (developmental sample).

4 contains 0.2% Melamine resin, American Cyanamid Company # 421.

5 contains 0.1% Durite, The Borden Company phenol furfural resin # S4120.

6 contains 0.1% Resorcinol resin, Schenectady Varnish Company # 1505-A.

7 contains 0.1% Lustrex, Monsanto Chemical Company latex resin # 201.

8 contains 0.1% Resinox, Monsanto Chemical Company liquid bonding phenolic # 468.

9 contains 0.1% Resimene, Monsanto Chemical Company melamine resin # 814, and contains also 0.25% catalyst, Monsanto Chemical Company's Resimene RA-032.

10 contains 0.1% Geon, B.F. Goodrich Chemical Company polyvinyl chloride-vinylidene chloride copolymer.

In the tables, H is Hydrochloric acid, A is Acetic acid, L is Lactic acid, and P is Phosphoric acid. Only concentrations of 2.0% and 5.0% acids were used in this series of tests.

TABLE 8a. ACID TEST RESULTS ON CONCRETE CUBES WHICH CONTAIN RESINOUS ADDITIVES.

SOLUTION	PERCENTAGE LOSS IN WEIGHT AFTER 1 DAY IMMERSION					
	ST	1	2	3	4	5
2.0% H	1.3	1.2	1.0	1.3	1.3	1.3
5.0% H	3.5	2.8	2.7	3.4	3.1	3.3
2.0% A	0.5	0.6	0.0	0.7	0.8	0.5
5.0% A	1.1	0.8	0.2	1.1	1.0	1.1
2.0% L	0.3	0.4	0.1	0.5	0.4	0.1
5.0% L	1.0	0.6	0.5	1.2	1.1	1.2
2.0% P	0.3	0.1	0.1	0.3	0.5	0.3
5.0% P	0.8	0.3	1.4	1.0	0.1	1.0

	ST	6	7	8	9	10
2.0% H	1.3	1.2	1.2	1.2	0.7	0.4
5.0% H	3.5	3.4	3.7	3.8	2.9	3.0
2.0% A	0.5	0.5	0.4	0.4	0.1	0.0
5.0% A	1.1	0.9	0.8	0.9	0.7	0.3
2.0% L	0.3	0.3	0.4	0.6	0.0	0.0
5.0% L	1.0	1.0	0.9	0.8	0.6	0.3
2.0% P	0.3	0.2	0.3	0.2	0.0	0.1
5.0% P	0.8	0.8	0.6	1.0	0.6	0.7

TABLE 8b. ACID TEST RESULTS ON CONCRETE CUBES WHICH CONTAIN RESINOUS ADDITIVES.

	PERCENTAGE LOSS IN WEIGHT AFTER 5 DAYS IMMERSION					
SOLUTION	ST	1	2	3	4	5
2.0% H	2.6	2.2	2.5	2.5	2.2	2.1
5.0% H	7.2	6.9	6.7	7.0	6.2	6.4
2.0% A	0.8	1.0	0.4	1.1	1.0	1.0
5.0% A	2.0	2.1	1.2	2.2	2.0	2.2
2.0% L	0.4	1.3	0.1	0.9	0.9	0.4
5.0% L	1.6	2.4	3.1	2.1	2.0	2.0
2.0% P	0.5	1.1	0.4	0.6	0.7	0.7
5.0% P	2.1	2.2	1.7	2.0	2.1	2.2

	ST	6	7	8	9	10
2.0% H	2.6	2.2	2.1	2.2	1.3	1.2
5.0% H	7.2	6.9	7.4	7.3	6.1	6.7
2.0% A	0.8	0.9	0.8	0.8	0.2	0.0
5.0% A	2.0	1.9	1.9	1.7	1.5	1.0
2.0% L	0.4	0.6	0.7	0.8	0.0	0.0
5.0% L	1.6	1.7	1.8	1.6	1.2	0.9
2.0% P	0.5	0.4	0.8	0.6	0.3	0.2
5.0% P	2.1	2.0	2.0	2.1	1.4	1.4

TABLE 8c. ACID TEST RESULTS ON CONCRETE CUBES WHICH CONTAIN RESINOUS ADDITIVES.

SOLUTION	PERCENTAGE LOSS IN WEIGHT AFTER 15 Days IMMERSION					
	ST	1	2	3	4	5
2.0% H	7.0	6.7	7.7	7.2	6.5	5.5
5.0% H	19.0	17.8	20.2	18.8	18.4	19.6
2.0% A	2.1	1.9	1.0	2.6	2.2	2.1
5.0% A	5.1	5.8	5.0	5.7	5.0	5.3
2.0% L	1.6	2.2	1.7	2.3	1.8	1.7
5.0% L	4.8	5.2	7.1	6.0	5.6	5.4
2.0% P	2.0	2.8	2.4	2.1	2.4	2.2
5.0% P	7.0	6.9	6.5	6.0	7.0	6.6

	ST	6	7	8	9	10
2.0% H	7.0	6.3	6.2	6.8	6.0	5.4
5.0% H	19.0	18.5	19.3	18.4	18.8	18.4
2.0% A	2.1	2.1	1.8	1.9	1.3	1.5
5.0% A	5.1	4.8	4.9	4.7	4.4	4.1
2.0% L	1.6	1.6	1.6	1.8	1.1	1.0
5.0% L	4.8	4.8	5.1	4.9	5.0	4.9
2.0% P	2.0	2.1	2.5	2.8	2.0	1.9
5.0% P	7.0	6.8	6.7	7.1	6.4	6.8

If one reads each line of this series of data horizontally across the page and remembers that the search is for general trends and not merely individual differences accounted for in the structure of each cube, one concludes that none of the resins tested offered any appreciable protection to the concrete from corrosion by acid.

Two series of cubes with polymeric additives were sent to us from Catskill. One of these contained ethyl cellulose with various concentrations of carbon tetrachloride included; and the other series contained polystyrene also with varying percentages of carbon tetrachloride. The figures for these acid test results were very similar to those presented in the preceding tables and since they were reported during the year, they are consequently not included here.

Part 7. Results on Continuous Flow Acid Tests.

In Figure 4 on Page 23, we have shown the apparatus used in conducting this test and we have described the test under "Apparatus and Procedure".

Two cubes of Anti-Bacterial Cement were used in these tests, one in 0.5% Hydrochloric acid, the other in 0.5% Acetic acid. The results of the test are given in Table 9, where a comparison is shown with the results of the test run statically, the normal way, using the same concentration of acids. In the table, <u>SF</u> indicates static conditions, and <u>CF</u> indicates Continuous Flow.

TABLE 9.. STATIC AND CONTINUOUS FLOW ACID TEST RESULTS.

	PERCENTAGES LOSS IN WEIGHT RECORDED AFTER					
	1 DAY		5 DAYS		15 DAYS	
SOLUTION	SF	CF	SF	CF	SF	CF
0.5% H	0.1	2.6	0.1	12.3	1.0	31.0
0.5% A	0.1	1.0	0.1	2.4	0.1	8.3

The rate of attack for Hydrochloric acid, continuous flow, appears to be from 25 to 30 times that of the static acid attack; and a comparative figure, at least, for Acetic acid, though the data for the static condition is rather uncertain here..

Part 8. Converted and Unconverted Resins in Concrete.

In Table 10 is a comparison, in terms of percentage loss in weight, between those cubes containing unconverted resins and those cubes which were exposed to elevated temperature in an effort to convert the resin they contained to its final form..

There are two kinds of cubes involved. Though each type contains 1.0% of resin by weight of the cement, the one which contained Melmac 480 as an additive was made with regular Portland cement, while the one which contained Phenolic SP 8023 was made with a floor topping mix of High Early Strength cement.

We used only 2.0% acids in the tests; and in the table, "U" denotes the unconverted series, or those cubes which were not exposed to heating, and "C" denotes those which were "converted by heat."

TABLE 10. ACID TEST RESULTS, CONVERTED AND UNCONVERTED CONCRETE CUBES.

2.0% ACID	TIME EXPOSED	PERCENTAGE WEIGHT LOSS 1.0% MELMAC U	 1.0% MELMAC C	 1.0% PHENOLIC U	 1.0% PHENOLIC C
H	1 day	2.2	2.3	1.0	0.4
A	"	0.0	0.9	0.0	0.5
L	"	0.2	0.6	0.1	0.9
P	"	0.3	1.3	0.1	0.1
H	5 days	6.0	7.1	2.5	1.6
A	"	0.0	1.6	0.4	1.3
L	"	0.5	1.7	0.1	1.1
P	"	1.2	3.1	0.4	0.4
H	15 days	20.4	22.8	7.7	6.5
A	"	1.7	2.7	1.0	2.0
L	"	2.3	3.4	1.7	1.8
P	"	5.5	7.6	2.4	1.8

We see that there is no great advantage or disadvantage developed as a result of the conversion by heat of the resin contained in the cubes. In the case of the Melmac 480, corrosion appears to be greater on the heated cubes, but the difference is not excessive in any case.

Two conclusions may be drawn from this set of data. Either the resins gave no added protection to the cubes even when converted, or the heating of the cubes increased their corrosion susceptibility to a greater extent than this susceptibility was decreased by the converted resin.

SUMMARY

During the year, tests were made on the components of various polymeric materials to determine the feasibility of their incorporation into cement, sand and water mixtures; this was done to try to improve certain properties of cement such as corrosion resistance, entrainment of air, workability and plasticity, etc. A great many partially converted resins were then requested from the industrial manufacturers of the products we desired. Unfortunately, only a small number of those requested could be secured within the time limits in which we were working; these were given a complete run of qualitative and semi and complete quantitative tests with cement, sand, and water mixtures. None of the samples secured, however, proved to be of substantial enough value in combination with cement to warrant the company's use of the substance as an interground additive to their cement products.

The field of resins and plastics is large, and we feel that, if explored sufficiently, a project of considerable length, it offers promise of a successful conclusion to many of the corrosion problems encountered in the use of concrete.

BIBLIOGRAPHY

(1) Haddan, H.J.; British patent # 9,381 (1909)-- "A Waterproofing Compound for a Portland Cement." cf, CA (Chemical Abstracts) 4, 821 (1910).

(2) Splittgerber, A.; Z. Wasserversorgung Abwasserkunde 7, 46-48, 51-55, 63-65 (1920). cf, CA 15, 4044 (1920).

(3) Frank, K. and Dietz, K.; U.S. patent # 1,818,888 (1931)-- "Acid Proofing Cementing or Lining Material." cf, CA 25, 5538 (1931).

(4) Sorkina, D.E.; Korrozia i Borba s Nei 5, No. 5-6, 24-33 (1939). cf, CA 36, 2107 (1942).

(5) Brick, B.R.; U.S. patent # 2,574,168 (1951)-- "Rendering Masonry Water Repellent." cf, CA 46, 1226 (1952).

(6) Suzuki, S.; Japanese patent # 1085 (1953)-- "Rapid Hardening and Water Resisting Agent for Cement." cf, CA 48, 1649 (1954).

(7) Brown, O.; Thesis, Department of Chemistry, Union College, Schenectady, N.Y. (1950).

(8) Dunbar, S.; Thesis, Department of Chemistry, Union College, Schenectady, N.Y. (1955).

(9) Bogue, R.H.; "The Chemistry of Portland Cement", Reinhold (1947).

(10) Mason, J.P. and Manning, J.F.; "The Technology of Plastics and Resins", Van Nostrand (1945).

(11) Simonds, H.R.; "Industrial Plastics", Pitman (1945).

(12) Richardson, H.M. and Wilson, J.W.; "Fundamentals of Plastics", McGraw Hill (1946).

(13) Modern Plastics Encyclopedia Issue; September, 1954; pub., Plastics Catalogue Corporation, Bristol, Conn.

(14) ASTM Standards on Cement; The American Society for Testing Materials, Philadelphia, Pa.; 1952 edition.

(15) Mason, J.P. and Manning, J.F.; cf, (10) above, Page 72.

(16) Simonds, H.R.; cf, (11) above, Page 30.

(17) Richardson, H.M. and Wilson, J.W.; cf, (12) above, Pages 1-25.