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## Increasing Sheet Strength by Partial Carboxymethylation

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## INCREASING SHEET STRENGTH

BY

## PARTIAL CARBOXYMETHYLATION

Submitted to Mr. Robert T. Elias

as partial fulfillment of the requirements

of the Pulp and Paper Curriculum,

Western Michigan College, Kalamazoo, Michigan

June 1, 1956



## TABLE OF CONTENTS

	<u>Page</u>
Abstract	1
Literature Survey	1
Introduction	1
History of Carboxymethylcellulose	2
Preparation of Carboxymethylcellulose	3
A. Alkali Cellulose	3
B. Carboxymethylcellulose	4
Properties of Carboxymethylcellulose	6
A. Physical	6
B. Chemical	10
Utilization in the Paper Industry	14
A. Beater Additive	14
B. Surface Application	16
Literature Cited	20
Experimental Outline	24
Purpose	24
General Procedure	24
Detailed Procedure	25
Equipment and Materials Needed for Experimental Work	29
Literature Cited	30

## TABLE OF CONTENTS

(continued)

Experimental Procedure	<u>Page</u> 31
Discussion of Results	34
Conclusions	37
Appendix	39
Table 1: Dry Sheet Strength Data	39
Table 2: Wet Sheet Strength Data	40
Graph I: Comparison of Dry Tensile Strengths	41
Graph II: Comparison of Dry Tear Strengths	42
Graph III: Comparison of Dry Fold Strengths	43
Graph IV: Comparison of Dry Mullen Strengths	44
Graph V: Comparison of Wet Tensile Strengths	45
Graph VI: Comparison of Wet Tear	46

## ABSTRACT

The objective of this thesis was to increase sheet strength by partial carboxymethylation of cellulose fibers. A survey of literature disclosed the fact this had been done in an alcoholic solution. An experimental procedure of partially carboxymethylating individual fibers in an aqueous solution was developed. It did not increase sheet strength and a second procedure was developed. In this method formed sheets were subjected to a carboxymethylation treatment. An evaluation of test data led to the following conclusions:

1. Dry and wet strength increases were obtained by treating a sheet with caustic.

2. The carboxymethylation procedure did not increase sheet strength, but a reaction did occur in the monochloroacetic acid bath.

3. Some dry strength increase shown by unneutralized caustic treated sheets was due to absorbed caustic.

4. Fiber shrinkage and swelling account for dry strength increases of neutralized CMC and caustic sheets.

5. Wet strength of the caustic treated sheets was not caused by absorbed caustic.

## INTRODUCTION

Cellulose is a natural long-chain polymer composed of glucose " building blocks." It exists as a fiber since it has a relatively inflexible chain, strong intermolecular forces, and a highly symmetrical configuration which readily forms a crystal lattice (1). Upon mechanical beating and subsequent drying, a slurry of such fibers will form fiber-fiber bonds which papermakers are constantly striving to improve. Although several theories exist, the nature of this phenomenon is not fully understood (2).

Cellulose (3) contains one primary and two secondary reactive hydroxyl groups per anhydroglucose unit. Its derivatives, mostly esters and ethers, are formed upon reaction of these groups with desired substitutes. The reaction is heterogeneous and thus, the products are not uniformly substituted (4). The usefulness of cellulose has increased enormously through formation of derivatives. Unlike cellulose, they often are water-soluble and have greater softness and flexibility (5). Many derivatives

have been prepared, but only a few are commercially significant. Included among the latter is the sodium salt of carboxymethylcellulose or NaCMC. Since the author is specifically concerned with NaCMC, readers desiring detailed information regarding cellulose derivatives are referred to excellent volumes by Ott (6) and Wise (7).

## HISTORY

Though proposed in 1905 (8), cellulose etherification was not accomplished until 1912 (9, 10). Following initial work by Lilienfeld (11) and others (12), many cellulose ethers, including NaCMC, were prepared. Jansen (13), a German chemist, is credited with the original preparation of NaCMC in 1916. He reacted alkali cellulose with monochloroacetic acid in an alcohol solution. Chowdhury (14) improved the process by preparing NaCMC in an aqueous solution. Hoppler (15) declared that commercial preparation was not as simple as the reaction carried out in the laboratory. The chief difficulty is the large reaction

volume which is very corrosive. Numerous patents have been issued since the first preparation of NaCMC. It is extremely versatile and used in many phases of industry (16). However, only applications of NaCMC in the paper industry will be presented later.

## PREPARATION

### A. Alkali Cellulose

Cotton linters and high alpha pulps are the raw materials for NaCMC. These are converted to alkali cellulose when placed in an 18 to 35 percent caustic solution (17). The alkali cellulose is pressed to remove excess alkali. The final product should have a press weight of about four since at least a two to one water-cellulose ratio is needed for ample swelling of the cellulose (18). Lorand (19) reported that alkali cellulose composition is extremely important for the following reasons:

1. The alkali-water ratio in its preparation affects speed of etherification.
2. The D.S. (degree of substitution) of the final product is dependent upon the cellulose-alkali ratio.
3. Extent of side reactions is established by the alkali-water ratio.

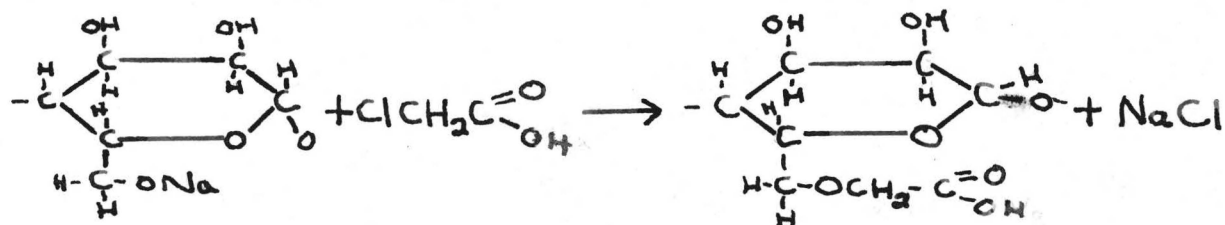
In order to reach the "potential reaction centers," the etherifying reagent must dissolve in the alkali and then diffuse into the fiber (19). Since the alkali cellulose serves to speed this diffusion by opening the fiber through swelling, one obtains higher D.S. as the caustic concentration increases (19). In addition to caustic, other bases (20), such as quaternary ammonia bases, can be used to treat the cellulose prior to etherification. However, their cost and degradative effect on cellulose favor the use of caustic in commercial operations (20).

#### B. Carboxymethylcellulose

Carboxymethylcellulose used commercially is the sodium salt or NaCMC. Other frequently used terms are "Carbose," cellulose gum, and cellulose glycolate. It is



prepared by reacting alkali cellulose with monochloroacetic acid according to the following equation:



The sodium carboxymethyl group replaces the hydrogen on the free-OH group. As each anhydrous glucose unit has three free-OH groups, it is possible to get a D.S. of three (17). Although uneven substitution will always occur, it is possible to prepare fairly uniform NaCMC containing minimum quantities of undesirable impurities (21).

NaCMC is commercially prepared by several manufacturers. The Kalle Company, a German concern, uses a batch process involving the treatment of sulfite pulp with 18 percent alkali to form alkali cellulose. This is mixed with sodium monochloroacetate for several hours and NaCMC is formed (17). Wyandotte (17, 22, 23) makes NaCMC by a continuous process of treating alkali sulphite pulp with monochloroacetic acid. Powdered cellulose is added to a rotating drum where it is sprayed with 35 percent caustic and then 78 percent monochloroacetic acid. It remains in the



chamber for about three hours before being removed. The NaCMC is aged for several more hours and dried for shipment. The Buckeye Cotton Oil Company (17, 22, 24) employs a continuous sheet of cotton linters which is sprayed with 15 percent hydrochloric acid, washed, dried, and sprayed with alkali and monochloroacetic acid. Finally, it is passed through carbon dioxide gas to neutralize the caustic. The NaCMC is ground prior to shipment.

## PROPERTIES

### A. Physical

Technical grades of NaCMC are cream colored, unsafe for human consumption, and slightly odorous due to impurities formed in the preparation reaction. Pure samples are white, odorless, tasteless, and non-toxic. Its solubility characteristics, as given by "The Encyclopedia of Chemical Technology " (25), are as follows:

1. Soluble in water if the D.S. (degree of substitution)

is over four-tenths.

2. Soluble in six percent caustic at approximately three-tenths D.S.

3. Soluble in six percent caustic ( $-10^{\circ}\text{C}.$ ) at one-tenths D.S.

Tappi Monograph No. 9 (21) differs somewhat from the preceding reference. It regards seven-tenths as the minimum D.S. for solubility in hot and cold water; two-tenths to seven-tenths D.S. as the range of solubility in five percent caustic; and two-tenths as the lowest D.S. for solubility in water solutions. Although solubility is chiefly determined by D.S., uniformity of substitution and chain length of the cellulose molecule do have some influence. For example, a uniformly substituted sample of three-tenths D.S. might be nearly soluble in water while a non-uniform one might have only partial solubility (26). Likewise, a short-chain product will be more soluble than a long-chain if the degrees of substitution are equal (14, 26). Oils and organic solvents usually will not dissolve NaCMC (27, 28). It is soluble in aqueous solutions containing about 40 percent acetone and a fifty-fifty mixture will form a viscous dispersion (27). However, it is insoluble in solutions which have more than 70 percent acetone.

Clear water solutions of NaCMC are most efficiently prepared if low concentrations, heated water, and "maximum stirrer shear" are used (28, 29). Tappi Monograph No. 9 (21) says that the temperature shouldn't be above 50 to 70°C., but Du Pont (28) states that it can safely lie in the boiling range. In either case, agitation must be used to avoid local overheating and subsequent discoloration (28). The agitation also serves to prevent formation of hard-to-destroy lumps which sometimes form as NaCMC is added to water. To provide additional protection against lump formation, the NaCMC is prewetted with non-swelling liquid before being placed in water (28, 29). Solutions will keep for several months if mold and bacterial growth are prevented. Formaldehyde, Dowicide, and pine oil are common preservatives that can be used (28, 29, 30).

Viscosity of NaCMC solutions is influenced by concentration, temperature, pH, and chain length of the cellulose molecule (21). Hoppler (15) reports that the amount of "closed wood" in the cellulose molecule during the preparation process is also a factor. Since high concentrations are too viscous, industrial solutions usually are below five percent solids (31). Like most solutions, beating will lower viscosity. Table I from Tappi Monograph No. 9 (21) shows the

pronounced effect of temperature. For maximum viscosity a

Table I

Effect Of Temperature On Viscosity  
Of A Two Percent NaCMC Solution

Temperature	Viscosity (centipoises)
5°C.	1,400
25°C.	550
75°C.	140

solution of NaCMC should have a pH of six to eight. Lowering the pH to four gives 25 to 50 percent drop while increasing it to 11 causes a ten percent drop (27). If the pH is less than three, insoluble cellulose glycolic acid precipitates (27, 28). Chain length of the cellulose molecule also affects viscosity. A long-chain sample will be more viscous than a similar product (21). Horsey (26) reports that different viscosity-type substances can be formed by degrading seven or eight-tenths D.S. NaCMC. However, a product of three-tenths

D.S. is not readily degraded. When measuring viscosity, one must adhere to a standardized procedure since NaCMC does not form a Newtonian solution (15, 28). Du Pont (28) and Hercules (29, 30) both specify the use of a Brookfield Viscometer for viscosity determinations. This instrument is preferred because it has a controllable rate of shear which is not true of capillary or falling ball viscometers (28). A viscosity reading depends on the following factors (30):

1. Uniformity of solution at a controlled temperature.
2. Concentration.
3. Rate of shear.
4. Degree of agitation prior to measurement.
5. Time factor between agitation and measurement.

From this, one realizes that several measurements must be made before a reasonably accurate viscosity reading is obtained (28).

#### B. Chemical

Since NaCMC is a cellulose derivative, it can enter

reactions analagous to those of cellulose (32). The unsubstituted hydroxyl groups can form esters or ethers. They may also form addition compounds with alkalies and complex salts or be oxidized to produce acid and aldehyde groups (32). The latter degradate the cellulose molecule and change most properties of a sample (32). Although NaCMC is not precipitated by alkali metal ions, it is only slightly soluble in their presence (27, 28). If lead, silver, mercury, iron, aluminum, nickel, or copper ions are added to a NaCMC solution, a carboxymethylcellulose salt precipitates (33). Some of these dissolve when ammonia or caustic are added (27). It is interesting to note that the salts of copper and nickel are blue, the ferric salt red, and the others colorless (33). Horsey (26) said that the salts of surface-type NaCMC (about seven-tenths D.S.) are usually more complex than those of the beater-type (three-tenths D.S.). Likewise, the beater-type precipitates more completely than the surface-type. The formation of insoluble metal salts by a double decomposition reaction is the foundation for several utilizations of NaCMC which will be discussed later (27, 32). Table II, taken from a Hercules (29) industrial bulletin, shows the effects which various salts produce on NaCMC solutions. They (29) concluded that the "salts of amphoteric multivalent metallic elements appear most likely to precipitate NaCMC.

Table II

Effect Of Salts On Two Percent NaCMC  
Solutions

Salt	Results	Effect Of Caustic On Precipitate
Magnesium chloride	No precipitate	-
Manganese sulfate	No precipitate	-
Calcium chloride	No precipitate	-
Aluminum sulfate	Precipitate	Soluble
Barium chloride	Fine precipitate	Soluble
Barium nitrate	Precipitate	Soluble
Stannous chloride	Precipitate	Soluble
Chromium nitrate	Precipitate	Insoluble
Silver nitrate	Precipitate	Insoluble
Ferric chloride	Precipitate	Insoluble
Ferrous sulfate	Fine precipitate	Insoluble
Lead acetate	Precipitate	Insoluble
Zirconium sulfate	Precipitate	Insoluble



Upon acidification of NaCMC below a pH of three, CMC (cellulose glycolic acid) is produced (29). Excess amounts of a strong mineral acid precipitate CMC (29). However, it is still soluble in a 25 percent solution of acetic acid (27). The exact pH at which a precipitate is formed depends on the degree of substitution and the acid used (29). For example, hydrochloric causes precipitation at a higher pH than nitric (29). "The Encyclopedia Of Chemical Technology (25)" states that CMC is formed by lowering the pH to two and one-half, but the presence of a water-miscible liquid, such as alcohol, is needed for precipitation. Hercules (29) reports that another method of preparing CMC is through the use of certain ion exchange resins which replace the sodium ions in NaCMC with hydrogen ions. Dispersions of CMC made in this manner are stable, salt-free, and suitable for film formation (29). CMC with a three-tenths D.S. is a fairly strong acid having an ionization constant approximately equivalent to acetic acid (32). Since it is an acid, CMC will react with alkalies and metal hydroxides (32).



## UTILIZATION IN THE PAPER INDUSTRY

### A. Beater Additive

Beater addition of NaCMC raises dry strength of paper (26). Several explanations for this exist. One concept (34) is that the carboxymethyl group opens the fiber structure to some degree and makes it more porous and easier to beat and fibrillate. The second theory (34) favors the idea that carboxymethyl groups create a pulp which is easily swelled by water. Also, the carboxymethyl groups protruding from the cellulose molecule aid bonding between adjoining fibers. Walecka (34) concluded that both theories probably were partially correct. Cottrall and Mark and others theorized dry strength was partially a function of fiber-fiber bonding and that free-OH groups in close contact tend to bond as water is removed (26). Pulps beaten to an intermediate freeness would have more free-OH groups than unbeaten pulps and consequently, develop more dry strength. An enlargement of the theory (26) is that addition of a substance which has more free-OH groups will increase dry strength at a predetermined freeness or obtain equivalent strength with less beating. A substance that can be retained and increase strength in

this manner is called a "pulp hydrating agent (26)."

Although the optimum point of addition is frequently the fan pump or headbox, NaCMC can be added to the beater as a powder or solution (27). It should be added at a high freeness if greatest strength improvements are to be obtained (21). Du Pont's Technical Bulletin (27) states that the NaCMC must be added and dissolved before alum in order to acquire maximum results. Laurell (35) found that best results were achieved when NaCMC was added after alum. As NaCMC is added, it causes the pulp to feel "slow," but the effect is mostly eliminated upon addition of alum (21). The alum forms an insoluble aluminum salt of NaCMC (27). Since NaCMC treated pulp is resistant to acid but not alkali treatment, "broke" is easily defibrated near a pH of nine (21). Alum precipitated NaCMC is easier to retain as the basis weight increases (26). Little NaCMC is retained unless enough alum is present to precipitate it (35). It was also found (35) that if equivalent amounts of alum are added, the lower substituted NaCMC is retained more than "conventional materials."

NaCMC is sometimes employed as a deflocculating agent (27). When used as such, it is added as a solution in the fan pump or headbox in order to avoid harsh mechanical action (27). About a one percent addition of NaCMC sucessfully deflocculates

long-fibered pulps (27). Best results are obtained when alum is not added and the stock flows onto the wire with as little turbulence as possible (27). Pollok (36) theorized that the mechanism for NaCMC's dispersing property could be the formation of a coating around each fiber which separates it from other fibers. Perhaps it also affects the electrokinetic forces (36).

#### B. Surface Application

Solutions of NaCMC can be applied at the size press or calender stack to improve the strength and printing properties of paper and paperboard (21). Since NaCMC is compatible with many fillers and water-soluble binders, it is suitable for numerous coating and sizing applications (27, 28). Tappi Monograph No. 9 (21) states that a calender application on nine to 30 "point" board can give a five to 20 percent increase in tensile and Mullen. The Paper Maker (37) reported that the average increase was ten to 12 percent. In both cases, best results were obtained from boards having a furnish of waste paper and deciduous and/or groundwood pulp (21, 37). Surface NaCMC treatments can also give nearly 30

percent increases in tear (21, 37). This is caused by the decreased jordaning needed to give a certain tensile and Mullen (37).

NaCMC treatments improve surface properties such as abrasion resistance, stiffness, and decreased fuzziness (27). It is particularly useful for gloss-ink printing (29). Printing of this type requires some retention of the vehicle in the dried surface film of the ink ("ink holdout") (30). Since proper treatments of NaCMC give a sheet oil resistance, adsorption of oil base inks is prevented and high gloss produced (27). Horsey (26) reported that packaging board treated at the calender with surface-type NaCMC provides more than the required oil resistance for gloss-ink printing. NaCMC treated board has produced gloss "substantially" above that obtained from similarly treated water-calendered stock (30). Hercules (30) reports a 41 percent gloss-ink saving on paperboard having less than a pound of NaCMC per 10,000 square feet.

To produce completely oil and grease resistant paper, a continuous protective film must be formed (27). Light applications of NaCMC do not create such a film (26). Consequently, liquids penetrate treated stock although not

as rapidly as in the case of untreated (26). Horsey (26) said that penetration time is directly proportional to the viscosity of the penetrating liquid if NaCMC is unaffected by the latter. A sheet is made more grease resistant by applying several coatings of NaCMC (26).

NaCMC is a good adhesive and can serve as a coating binder (21, 27, 29). Since it is compatible with so many substances used as binders and fillers, NaCMC is suitable for a wide range of sizing and coating applications (28). Its presence in a coating mixture is desirable for the following reasons:

1. The settling tendency of pigment dispersions is lowered (27).
2. Control over viscosity and flow properties of the coating colors is increased (29).
3. Formation of streaks during coating of "free papers" is prevented (29).

Pollok (36) emphasized the fact that coatings containing NaCMC must be treated with alum. This precipitates the insoluble aluminum salt and gives the coating wet rub resistance (36).

NaCMC improves efficiency of calender coloring by increasing viscosity of the coloring mixture (27). Tappi

Monograph No. 9 (21) reports that one or two pounds of NaCMC per 100 gallons of coloring solution greatly enhances the appearance of a surface colored sheet. It can be used with acid and direct dyes, but generally is non-compatible with basic dyes (21, 27). NaCMC is also used in deinking waste news stock (27). A much lighter color is obtained when a one percent solution is added to a hot water or alkali slurry of news (27). The NaCMC suspends the dirt particles which are then easily washed out (27).

One should note that a single application technique will not necessarily bring about the improvements which have been mentioned (37). The type most effective for a given use is determined by the following factors (37):

1. Amount of treatment.
2. Furnish.
3. Sizing.
4. Density
5. Finish of the sheet to be treated.
6. Equipment for application.
7. Operation speed.

"The Paper Maker" (37) states that its results have been "obtained repeatedly by the proper type of NaCMC surface application."

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## EXPERIMENTAL OUTLINE

### Purpose

The purpose of this thesis is to determine the influence on sheet strength of partially carboxymethylated pulp. Beating time for the treated fibers will be varied so that their rate of strength development can be compared with that of untreated pulp.

### General Procedure

Cotton fibers will be partially carboxymethylated by a reaction with caustic and monochloroacetic acid. Their influence on sheet strength is to be determined by six Valley laboratory beater runs. Three will have a 25 percent treated cotton and 75 percent bleached kraft furnish. The

others will be duplicate control runs in which the treated cotton fiber is replaced with untreated. The treated cotton will be added to the beater furnish at various degrees of beating. It is expected this will show that they develop strength faster than untreated fibers. Tappi Standards are to be followed for Canadian Standard Freeness and handsheet preparation at regular intervals of beating. After conditioning in an RH room, the handsheets will be tested for burst, tensile, tear, and fold. Data are to be graphed and tabled for discussion of results.

#### Detailed Procedure

Cotton fibers will be carboxymethylated until they are slightly water-soluble. However, no drastic change in fiber structure is desired. Only a few carboxymethyl groups are to be added to the cellulose chain with the hope that these will increase fiber-fiber bonding and dry strength. About 270 gms. of treated pulp are required for the experimental work planned. In addition, 270 gms. of unsubstituted pulp are needed for control purposes. The

carboxymethylated pulp will be prepared by adding 14.2 gms. of monochloroacetic acid to 270 gms. of alkali cellulose. Theoretically, this is enough for a three percent substitution. Since the author wants the fibers slightly water-soluble, it was decided to exceed the two percent substitution at which carboxymethylcellulose begins to dissolve (1). Unfortunately, time will not permit a quantitative determination of the degree of substitution actually obtained. The composition of the alkali cellulose has a great influence on the etherification reaction (2). It is to be prepared by swelling the cotton pulp in a strong caustic solution for one hour before the acid is added. In order to make a concentrated alkali solution, 120 gms. of caustic will be dissolved in water and diluted to 350 cc. This is a large excess of caustic for the reaction (3), but it will take the specified volume of concentrated solution to slurry 270 gms. of pulp. The monochloroacetic acid will be dissolved in water (25 cc.) and added dropwise from a separatory funnel to the alkali slurry of fibers. A mixer will agitate the slurry while the acid is being added. The slow addition is planned to take three hours and enable the reaction to go to completion. The corrosive nature of the reaction mixture necessitates the use of a glass beaker throughout the reaction. Due to the low degree of

substitution, no attempt will be made to control temperature. The treated pulp is to be washed with a 70 percent aqueous solution of methanol following carboxymethylation. This solution will precipitate any dissolved carboxymethyl-cellulose while removing water-soluble impurities. The 270 gms. of control pulp will be treated in the same manner as the carboxymethylated pulp except for the fact that no monochloroacetic acid is to be added.

The influence of partially carboxymethylated pulp on sheet strength will be determined by six Valley laboratory beater runs. Three will have a 75 percent bleached kraft and 25 percent partially carboxymethylated cotton furnish. The others are to be controls in which the treated pulp is replaced by untreated. The above furnish was chosen so that enough carboxymethylated fiber would be present to influence sheet strength. Bleached kraft was arbitrarily specified as time will not permit experimental work with other pulps. The treated fibers will be added to the beater at different stages of beating. It is anticipated this will show that they develop strength faster than untreated fibers. In the first beater run, addition is to be carried out before beating; in the second after 15 minutes of beating; and in the third after 40 minutes. Alum (        ) is to be



added with the treated pulp in order to precipitate the water-soluble carboxymethylcellulose. A duplicate control will be made for each of the beater runs described above. In these the treated cotton fibers are replaced by untreated pulp. Since it is difficult to consistently beat down to a standard freeness, time has been chosen as the standard unit of beating. Therefore, handsheets for all beater runs are to be made after zero, five, ten, 15, 20, 30, 40, and 60 minutes of beating. Canadian Standard Freeness will be checked at the same time. When the handsheets have been conditioned in an RH room, the following tests will be run: burst, tensile, tear, and fold. Handsheet preparation and all strength tests will follow Tappi Standards. Data from the tests will be graphed and tabled for discussion of results.

The total time available for the experimental work outlined is 17 Monday afternoons from one to five p.m. Thus, the following time allowances have been made:

1. Three Monday afternoons for preparation of the partially carboxymethylated pulp.
2. Six Monday afternoons for the beater runs.
3. Three Monday afternoons for testing handsheets.
4. Three Monday afternoons for writing-up results

5. Two Monday afternoons for a safety margin.

It is hoped that the experimental work will be done by March 30, 1956.

Equipment And Materials Needed

For Experimental Work

1. One pound purified monochloroacetic acid.
2. 540 gms. of high-grade cotton pulp.
3. 1620 gms. of bleached kraft pulp.
4. 120 gms. of caustic pellets.
5. One Valley laboratory beater and accessories.
6. One Canadian Standard Freeness tester.
7. One British sheet mold, press, and several sheet rings.
8. One tensile tester.
9. One tear tester.
10. One Mullen tester.
11. One MIT fold tester.
12. One RH room
13. One mixer (electric).
14. One 1 liter glass beaker.



15. One 1 liter glass graduate.
16. One separatory funnel.
17. One 250 cc. glass beaker.
18. One wide mouth bottle with top.
19. Dowicide for preserving the treated pulp.
20. Alum (        ).
21. One balance for weighing.
22. One lab book for data.

#### Literature Cited

1. Walecka, J., Proceedings of the 19th Executive's Conference, Institute of Paper Chemistry, Appleton, Wis., pages 11-15 (May 26-27, 1955).
2. Lorand, E. J., Ind. Eng. Chem. 31, No. 7: 891-897 (July, 1939).
3. Reasor, G. Personal interview, Hercules Powder Co., Kalamazoo, Michigan.

## EXPERIMENTAL PROCEDURE

The objective of this thesis was to increase sheet strength by partial carboxymethylation of cellulose fibers. An experimental procedure of carboxymethylating individual fibers was devised, but did not increase sheet strength. A second procedure using formed sheets for carboxymethylation was successfully developed.

The experimental work of this thesis was not carried out by the method described in the experimental outline. Partial carboxymethylation was accomplished by the standard procedure:

1. Single sheets of W. and R. Balston Genuine No.1 filter paper were placed in a 20 percent by weight caustic bath for 15 seconds.
2. The sheets were transferred from the caustic bath to a 60 percent by weight monochloroacetic acid bath where they remained for 60 seconds.
3. The treated sheets were removed from the monochloroacetic acid bath and placed in a water bath

for several minutes.

4. After the water wash, the sheets were pressed and dried on a Noble and Wood press and dryer.

5. Dry strength of the treated sheets was determined according to Tappi Standards T 423m-50, T 403m-53, T 404m-59, and T 414m-49. The sheets were conditioned in an RH room prior to testing.

6. Except for a 30 minute soak in distilled water (20 C), wet strength tests were carried out in accordance with Tappi Standards T 404m-50, and T 414m-49.

The baths used for the experimental work were 10x24 inch Pyrex glass baking dishes having a depth of two inches. These were lined up beside each other in order to minimize handling of the sheets being treated. The baths contained solutions of technical grade caustic and reagent grade monochloroacetic acid. The 60 percent by weight solution of monochloroacetic acid was prepared by dissolving 150 grams of acid in water and diluting to 250 cc. Likewise, the 20 percent by weight caustic solution was made by dissolving 50 grams of caustic in water and diluting to 250 cc. The monochloroacetic acid solution was seldom replaced as the treated sheets did not absorb it. However, the caustic was rapidly absorbed by the cellulose fibers and had to be

continuously replaced by new solutions. An electric timer measured the time a sheet was in each bath and prevented variations from the standard procedure. No attempt was made to follow or control reaction temperatures in each bath

Untreated and caustic treated controls were prepared for comparison with the carboxymethylated (CMC) sheets. The untreated controls received no treatment while the caustic controls soaked for 15 seconds in 20 percent by weight caustic. The caustic controls had to be air dried as they charred when heat dried. In the process of air drying between blotters it was noticed that the caustic controls bonded tightly to the blotters. Dry and wet strength testing procedures for all the controls duplicated those outlined for the CMC sheets.

In order to obtain test sheets from which all caustic had been removed, it was necessary to add an acid neutralization bath in the preparation of the CMC sheets and caustic controls. The acid bath was made by continuously passing carbon dioxide from a Kipp generator into a dishpan filled with water. Except for addition of the carbonic acid bath, the carboxymethylation treatment followed the standard procedure. After the monochloroacetic acid bath, the CMC sheets were transferred into the carbonic acid and kept there until



they were neutralized. The caustic controls were placed in a 20 percent by weight caustic bath for 15 seconds and then neutralized in the carbonic acid. Universal indicator tests were used to determine when the sheets were completely neutralized. Conditioning and testing of the sheets were carried out according to the standard procedure.

#### DISCUSSION OF RESULTS

As shown in Tables 1 and 2, dry and wet strength increases were obtained by preparing CMC sheets as described in the experimental procedure. Dry tensile, tear, fold, and Mullen of the CMC sheets are considerably higher than those of the untreated controls. It is observed that the caustic controls had similar strength increases. Before discussing the test data, units of the tensile and tear readings should be defined. Tensile tests were run on 4x0.5 inch strips and results are given in pounds. Tear data are given in terms of grams of force required to tear a single sheet.

The data illustrated by Graphs I, II, III, and IV show the unneutralized caustic controls have the greatest dry strength. However, it should be remembered that absorbed caustic gave these controls a 20 percent increase in sheet weight over the untreated controls while alkali swelling decreased sheet size by 20 percent. The strength increases of unneutralized CMC sheets were slightly less than the unneutralized caustic controls. Although the caustic in these sheets was partially neutralized by the monochloroacetic acid bath, sheet weight was 15 percent greater than that of the untreated sheets. The CMC sheets also had the same decrease in sheet size as the caustic controls. This decrease in sheet size and increase in relative sheet density was true of all CMC sheets and caustic controls. It serves as a partial explanation for increased dry strength shown by both neutralized and unneutralized CMC sheets and caustic controls.

Complete neutralization of the caustic controls with carbonic acid brought about a 40 percent decrease in dry strength. The carbonic acid removed 0.40 grams of absorbed caustic and lowered sheet weight so that it equaled the weight of the untreated control. Neutralization of the CMC sheets caused strength decreases proportional to those of the caustic controls. Likewise, sheet weight was lowered to that of the untreated control. These results prove that a

portion of the dry strength increases in the unneutralized CMC sheets and caustic controls was due to absorbed caustic in the sheet. It is interesting to note Graphs I, II, III, and IV show neutralized caustic controls had more dry strength than neutralized CMC sheets.

As shown by Graphs V and VI, untreated controls had negligible wet strength while CMC sheets and caustic controls had considerable wet strength. It was anticipated that the CMC treatment would increase wet strength, but developing wet strength by merely treating a sheet with caustic was unexpected and very surprising. Graph V shows a wet tensile of 1.25 pounds for the unneutralized CMC sheets and 1.10 pounds for the unneutralized caustic controls. Graph VI shows a wet tear of 36 grams for the unneutralized CMC sheets and 26 grams for the unneutralized caustic control. This indicates that most of the wet strength was caused by the caustic bath. However, CMC sheets did have slightly more wet strength than the caustic controls thereby showing the monochloroacetic acid bath was not totally ineffective.

Neutralization of the CMC sheets caused wet tensile to drop 30 percent and wet tear 60 percent. The carbonic acid removed something which gave wet strength to the sheet. A



filament forming compound was isolated, but not identified. This may have been responsible for the wet strength as it was insoluble in caustic and soluble with difficulty in water. It is important to note that the neutralized caustic control had the same wet strength as the unneutralized. As shown in Graphs V and VI, the neutralization procedure did not influence wet strength as it did in the case of the CMC sheet.

#### CONCLUSIONS

An evaluation of the test data led to these conclusions:

1. The caustic bath was responsible for the observed dry strength increases. Caustic control sheets had dry strengths equal to or greater than sheets which were treated with caustic and monochloroacetic acid.

2. A portion of the dry strength increases shown by the unneutralized CMC sheets and caustic controls was due to absorbed caustic. Neutralization caused large percentage decreases in the strength

of these sheets.

3. Dry strength increases shown by neutralized CMC sheets and caustic controls can be attributed to alkali swelling and shrinking which increased the surface area of the fibers and drew them closer together.

4. Wet strength shown by the caustic controls and CMC sheets was mainly a result of the caustic bath. However, CMC sheets did have slightly more wet strength than the caustic controls. The development of wet strength by a caustic treatment remains unexplained. From the theoretical point of view the explanation for the ability of caustic to create wet strength might give more insight into the nature of fiber bonding. Such an explanation is beyond the scope of this thesis.

5. Wet strength of the caustic treated sheets was not caused by absorbed caustic. Neutralized and unneutralized caustic controls had equal wet strength.

6. Although the monochloroacetic acid bath did not substantially increase sheet strength, it should not be automatically concluded that no reaction occurred when caustic sheets were placed in the acid. The data show that neutralization did not influence wet strength of the caustic controls while CMC sheets suffered decrease in wet strength. This indicates that a reaction did occur in the monochloroacetic acid bath.

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APPENDIX  
OF EXPERIMENTAL  
DATA

TABLE 1

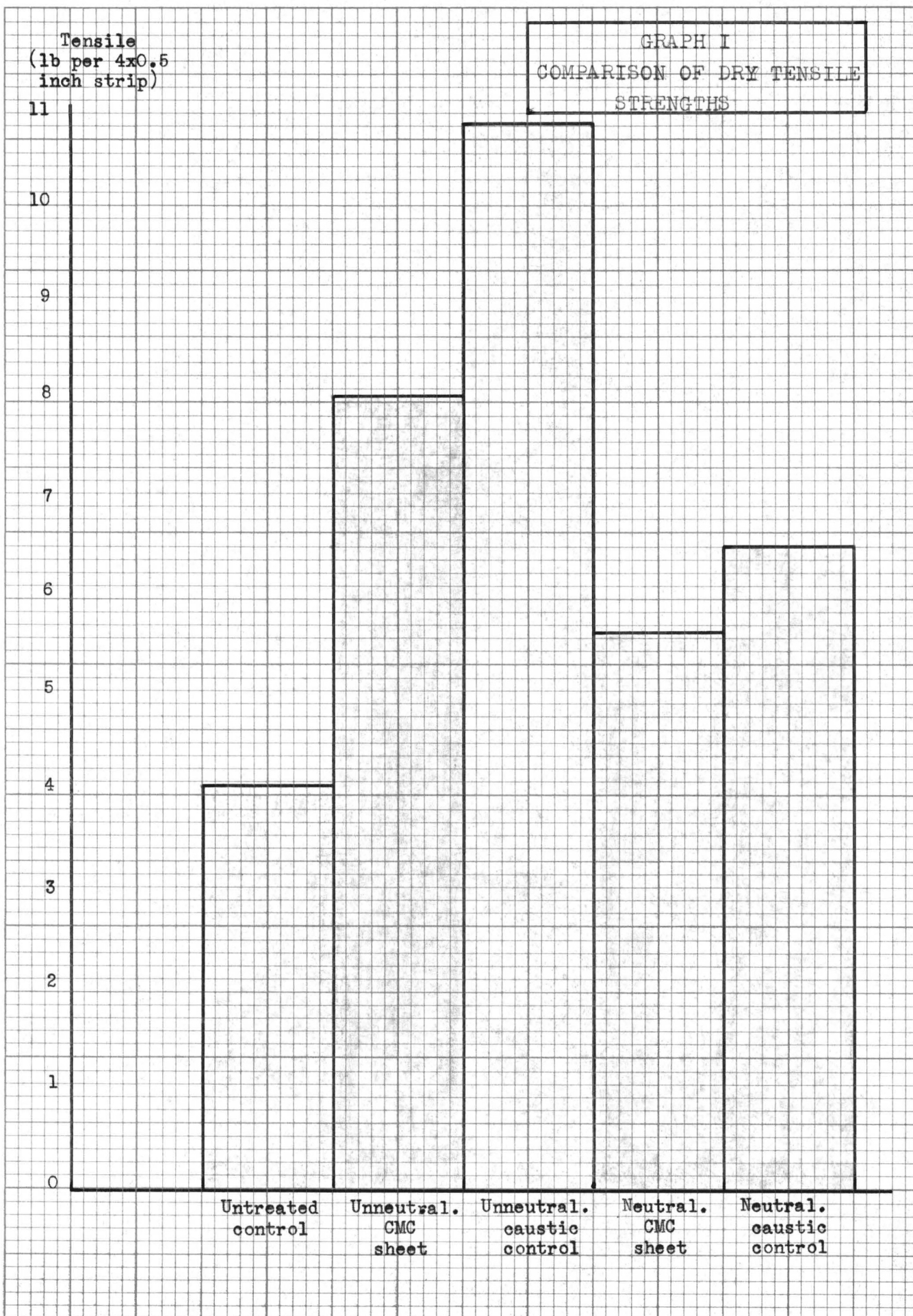
## Dry Sheet Strength Data

Type of sheet	Sheet weight (gm)	Tensile (lb per 4x0.5 inch strip)	Tear (gm per sheet)	MIT fold (double folds)	Mullen (p.s.i.)
Untreated control:	2.28	5.14	57.7	4.2	13.30
Unneutralized CMC sheet:	2.51	8.05	108.1	22.9	28.60
Unneutralized caustic control:	3.00	10.80	120.8	36.2	36.45
Neutralized CMC sheet:	2.28	5.68	79.0	-	20.53
Neutralized caustic control:	2.28	6.57	98.0	-	19.93

TABLE 2

## Wet Sheet Strength Data

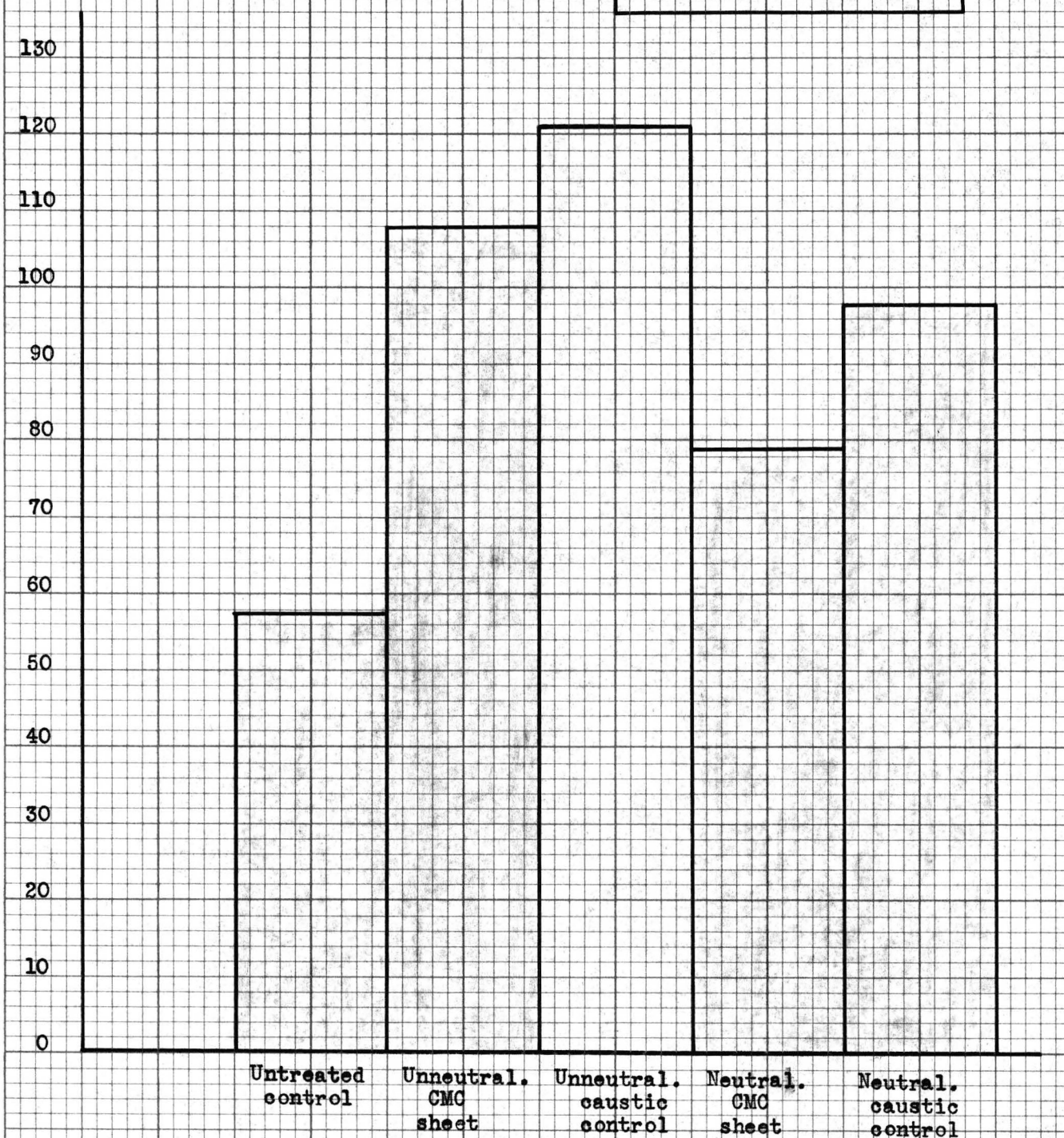
Type of Sheet	Tensile (lb per 4x0.5 inch strip)	Tear (gm per sheet)
Untreated control:	0.00	2.8
Unneutralized CMC sheet:	1.25	34.0
Unneutralized caustic control:	1.14	26.0
Neutralized CMC sheet:	0.87	14.48
Neutralized caustic control:	1.11	22.4





Tear  
(gm per sheet)

GRAPH II  
COMPARISON OF DRY TEAR  
STRENGTHS





MIT fold  
(double folds)

GRAPH III  
COMPARISON OF DRY FOLD  
STRENGTHS

40

35

30

25

20

15

10

5

0

Untreated  
control

Unneutral.  
CMC  
sheet

Unneutral.  
caustic  
control

Mullen  
(p.s.i.)GRAPH IV  
COMPARISON OF DRY MULLEN  
STRENGTHS

40

35

30

25

20

15

10

5

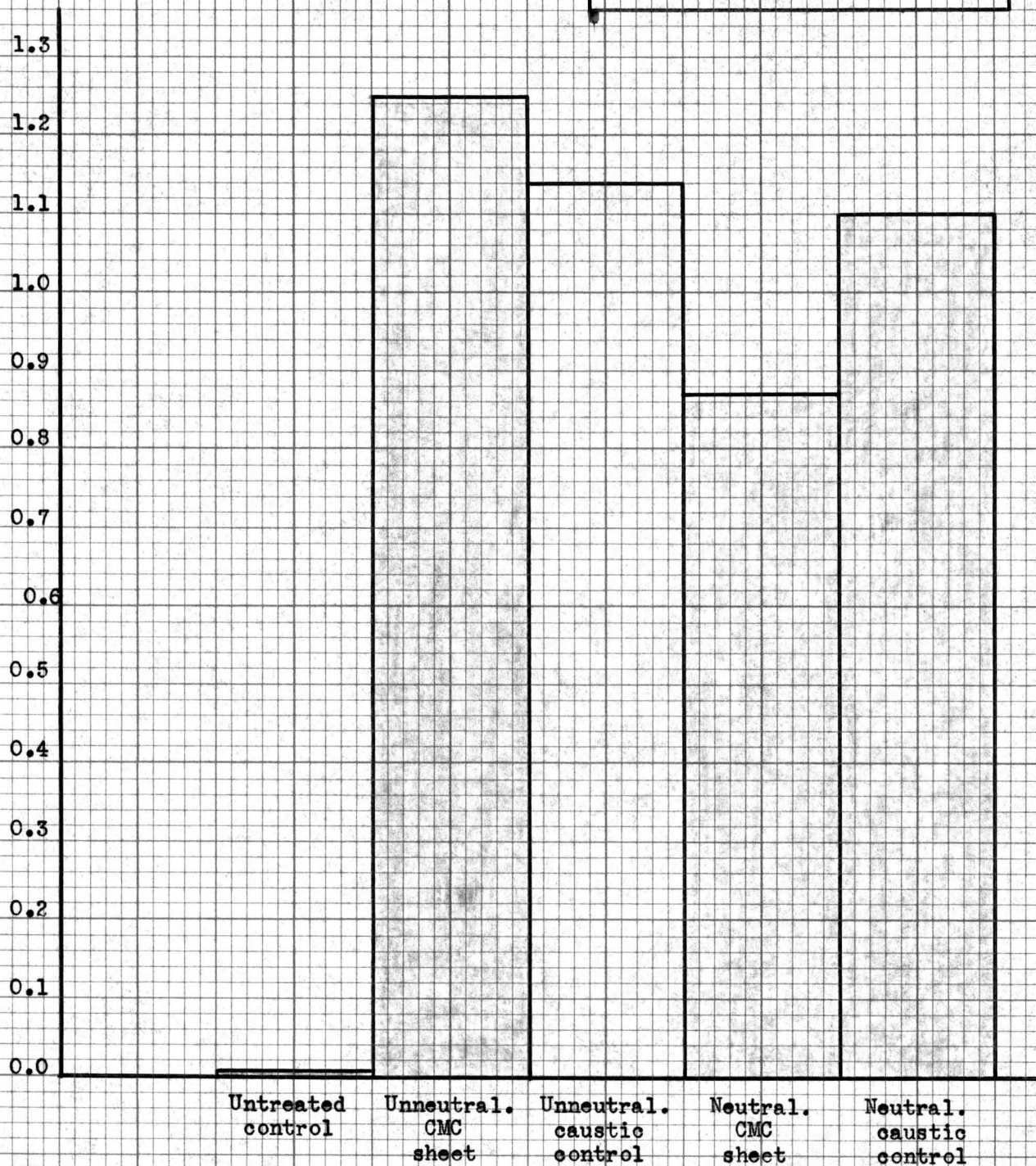
0

Untreated  
controlUnneutral.  
CMC  
sheetUnneutral.  
caustic  
controlNeutral.  
CMC  
sheetNeutral.  
caustic  
control



Tensile  
(lb per 4x0.5  
inch strip)

GRAPH V  
COMPARISON OF WET TENSILE  
STRENGTHS



Tear  
(gm per sheet)

GRAPH VI  
COMPARISON OF WET TEAR  
STRENGTHS

