

PROJECT REPORT FORM

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PROJECT NO. 1857
COOPERATOR I. P. C.
REPORT NO. Seven
DATE July 15, 1959
NOTE BOOK 1593
PAGE 110 TO 119
SIGNED C. Y. Chu

POSSIBLE METHOD OF INCREASING ABSORBENCY OF WOOD PULP PRODUCTS

INTRODUCTION

From the results shown in Project Report Six, it was decided to use a higher percentage of alkyl aryl sodium sulfonate in combination with blood albumin as an additive in the handsheets using the following three methods:

(1) By maintaining the concentration of complex the same throughout the sheetmaking process, i.e., the same concentration of complex in the mixer as in the deckle.

(2) By using the same concentration of complexes in the mixer, as above, then diluting in the deckle without readjusting the concentration of additives.

(3) By beginning with a concentrated solution, then diluting to the level as in first method while the sheet is being formed.

From the results of these three trials, it might be possible to get a better picture of the efficiency of this complex film in counteracting the self-sizing problem.

EXPERIMENTAL PROCEDURES

The preparation of a soluble protein-surfactant complex and the absorbency tests on original and aged samples of this work were made the same as in Project Report Six, except that the additions of the complexes to the handsheets were made in the following manner. In sample 2, the concentrations of additives were maintained at 0.0125% LR502-16 and 0.025% Blood Albumin to the solution in 0.5% consistency stock and in the deckle box where the consistency of the stock was diluted to approximately 0.04%. Then 52.2 g. oven-dried beaten pulp were measured into a stainless steel pail and diluted to 0.5% consistency with deionized water. Addition of 130 cc. of 1% LR502-16 was made to the slurry followed by 261 cc. of 1% Blood Albumin. The mixture was stirred for five minutes after each addition with a Lightnin' stirrer, and finally, 20 cc. of 1% alum solution was added and stirring was continued for another five minutes. An equivalent weight of 2.61 g. of such prepared stock was measured out and diluted to approximately 0.04% consistency in a deckle box. For maintaining the same concentrations of additives in the deckle box as in the mixing pail, 71.5 cc. of 1% LR502-16, 143 cc. of 1% Blood Albumin, and 11 cc. of 1% alum were added to 5.7 liters of additional water in the deckle before the fiber was poured in. Samples no. 3 and 4 were prepared in the same manner as sample 2, omitting protein in sample 3 and protein and surfactant in sample 4. In sample 5, the concentrations of additive at 0.5% consistency slurry were the same as in sample 2, 0.0125% LR502-16 and 0.0250% Blood Albumin to the solution. However, there were no additives added to the additional water in the deckle box. Samples 6 and 7 were prepared in the same manner as sample 5, omitting protein in sample 6 and protein and surfactant in sample 7. In sample 8, 0.15% LR502-16 and 0.030% Blood Albumin to the solution were added to the stock at 0.5% consistency and then

diluted to 0.0125% LR502-16 and 0.025% Blood Albumin in the deckle box. Additions of 1560 ml. of 1% LR502-16, 3120 ml. of 1% Blood Albumin, and 234 ml. of 1% alum were made to 52.2 g. oven-dried weight of 0.5% consistency pulp by above order, and the mixture was stirred for five minutes after each addition. An equivalent weight of 2.61 g. of this 0.5% consistency stock was measured and diluted to 0.04% consistency in the deckle box. Samples 9 and 10 were controls to sample 8. They were prepared in the same manner as sample 8, except in the absence of protein and of protein and surfactant, respectively.

In samples 2, 5, and 8, alum was added to the furnish at the ratio of 1:20 to the complexes present in that system. The amount of alum in the control samples was followed the same as their original formulas. Twenty-eight 2.61 g. sheets were prepared for each sample. Eight sheets from each sample were used for the fluorescence size test. They were divided into four groups and aged at 105°C. for 0, 1, 3, and 5 hours. The other 20 sheets from each sample were used for physical strength tests. They were also divided into four groups and aged at 105°C. for 0, 1, 3, and 5 hours (these samples were put in a glass tray and covered with a 1/4-inch thick glass plate while they were aged in an oven.

RESULTS AND DISCUSSION

CALIPER

There were two factors responsible for the thickness change in the sheets; (1) basis weight and (2) the additive. In this work, an attempt was made to maintain the same basis weight for all samples. The calipers of samples 2, 5, and especially 9 were slightly higher than other samples. (See Table I.). They were due to the presence of surfactant in the sheet. Sample 7 had a lower basis weight and, therefore, had a lower caliper.

APPARENT DENSITY

The apparent density was calculated by dividing the basis weight of the paper by the caliper of the sheet. Being inversely proportioned to the thickness, the density is dependent on the caliper for any constant basis weight. There were no significant changes in apparent density except for sample 9 which had a lower density. This might be due to the debonding effect of large quantities of the surfactant present.

BURSTING STRENGTH

This is a complex function of tensile strength and stretch giving an indication of the elasticity on toughness of the paper. Here again, there were no significant changes on samples 1 through 7. Samples 8 and especially 9 were found to be much lower in bursting strength than the others. This was an indication that the interfiber bonding of the sheet was affected by the presence of surfactant. Sample 10 also had lower bursting strength values than the other two alum controls, i.e., samples 4 and 7. This was due to the large amount of alum added and may be partly due to the fact that sample 10 was made from a different batch of pulp which might be slightly different in nature.

TABLE I

THE EFFECT OF ADDITIVE AND AGING ON PHYSICAL PROPERTIES
AND ABSORBCY TEST OF A SULFITE PULP

Sample No.	Additive ¹	Aging Condition at 105°C., hr.	Basis wt., lb. 25x40/500	Caliper, mils	Apparent Density	Mullen Bursting Strength, points	Elmendorf Tear, g./sheet	Tear Factor lb./in.	Instron Tensile, lb./in.	Fluorescence Size, sec.
1	None	0	46.4	3.6	12.9	62.0	41	0.88	33.5	5
		1	46.5	3.7	12.6	60.0	38	0.82	37.0	13
		3	47.1	3.6	13.1	60.6	44	0.93	35.0	47
		5	46.1	3.6	12.8	60.7	37	0.80	34.5	58
2	0.0125% LR502-16 (to the soln.)	0	49.1	3.9	12.6	59.6	43	0.88	33.0	7
		1	49.1	3.9	12.6	62.7	44	0.90	35.0	7
		3	49.2	3.8	12.9	58.3	42	0.85	33.5	10
		5	48.5	3.7	13.1	60.7	42	0.87	34.0	11
3	0.0125% LR502-16 (to the soln.)	0	48.0	3.8	12.6	63.4	43	0.90	37.5	14
		1	48.1	3.8	12.7	58.2	44	0.91	33.5	21
		3	48.6	3.7	13.1	61.4	42	0.86	36.5	48
		5	48.6	3.7	13.1	54.0	38	0.78	32.5	60
4	Alum	0	47.5	3.6	13.2	62.8	39	0.82	36.5	14
		1	45.9	3.4	13.5	61.1	36	0.78	37.0	11
		3	46.6	3.5	13.3	63.6	37	0.79	38.0	27
		5	47.2	3.5	13.5	58.4	36	0.76	36.0	66
5	0.0125% LR502-16 (to the soln.)	0	49.1	3.8	12.9	62.1	43	0.88	36.5	6
		1	48.6	3.7	13.1	63.4	41	0.84	35.5	6
		3	48.3	3.7	13.1	63.5	41	0.85	35.5	16
		5	46.9	3.4	13.8	60.0	42	0.90	38.0	30
6	0.0125% LR502-16 (to the soln.)	0	46.8	3.5	13.4	62.2	41	0.88	36.0	8
		1	47.6	3.6	13.2	64.1	39	0.82	35.0	6
		3	47.2	3.7	12.8	63.9	40	0.85	36.0	22
		5	46.3	3.7	13.5	60.6	39	0.84	36.0	52
7	Alum	0	45.0	3.3	13.3	60.3	38	0.83	35.0	9
		1	45.5	3.3	13.3	60.4	38	0.82	35.0	13
		3	45.0	3.4	13.6	60.0	38	0.84	35.5	40
		5	44.3	3.3	13.4	59.1	38	0.82	35.5	55
8	Alum	0	45.4	3.3	13.3	60.3	38	0.83	35.0	9
		1	45.0	3.3	13.3	60.4	38	0.82	35.0	13
		3	45.0	3.4	13.6	60.0	38	0.84	35.5	40
		5	44.3	3.3	13.4	59.1	38	0.82	35.5	55
9	Alum	0	45.4	3.3	13.3	60.3	38	0.83	35.0	9
		1	45.0	3.3	13.3	60.4	38	0.82	35.0	13
		3	45.0	3.4	13.6	60.0	38	0.84	35.5	40
		5	44.3	3.3	13.4	59.1	38	0.82	35.5	55
10	Alum	0	47.8	3.8	12.6	61.8	41	0.86	36.0	6
		1	48.0	3.8	12.5	57.7	36	0.76	36.0	16
		3	44.7	3.5	12.8	47.5	28	0.62	36.0	26
		5	45.3	3.6	12.9	42.6	26	0.54	36.0	52

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Instantaneous

¹See detailed procedure for addition.

TEAR

Tearing resistance is directly related to fiber treatment, inversely related to bursting strength and density, and is a measure of the amount of fiber length reduction. The results indicate that in sample 9 a considerable amount of surfactant was present in place of the fibers; i.e., the amount of fiber length was reduced more than in other samples, resulting in a lower tear resistance.

TENSILE STRENGTH

Tensile strength is a measure of the resistance of paper to direct tension, a component of the more complex bursting, folding, and tearing strength. It is defined as the force required to break a strip of paper having a specified length and a 15 mm. width. Samples 8 and 9 showed lower tensile values. This is understandable because of the large quantity of surfactant present. This caused a change in the amount and quality of fiber bonding and naturally, changed the tensile strength. Generally, the additives in samples 2 and 5 and their controls did not cause any serious effect in the physical properties of sheets compared to sample 1. In samples 8 and 9, however, a large quantity of surfactant present in the fiber caused a deterioration of physical strength to a great extent.

FLUORESCENCE SIZE TEST

In general, the loss of absorbency increased as aging proceeded. With exception of sample 9 which suffered a loss of too much physical strength, samples no. 2 and 8 gave the best fluorescence size test results. However, they were almost too costly to stop the loss of absorbency in these ways. Sample 5 had a better fluorescence size test at the end of five hours aging than all of the controls (see Fig. 1). The loss of absorbency was approximately only half that of the controls.

FUTURE WORK

Because of the favorable results obtained from this and previous works, it is suggested that the project be continued to study the efficiency of a film having the composition of 2.5% LR502-16 plus 5% Blood Albumin based on the weight of the fiber. This film should be studied after aging in two ways; by accelerated aging at 105°C. and by natural aging over a two-year period.

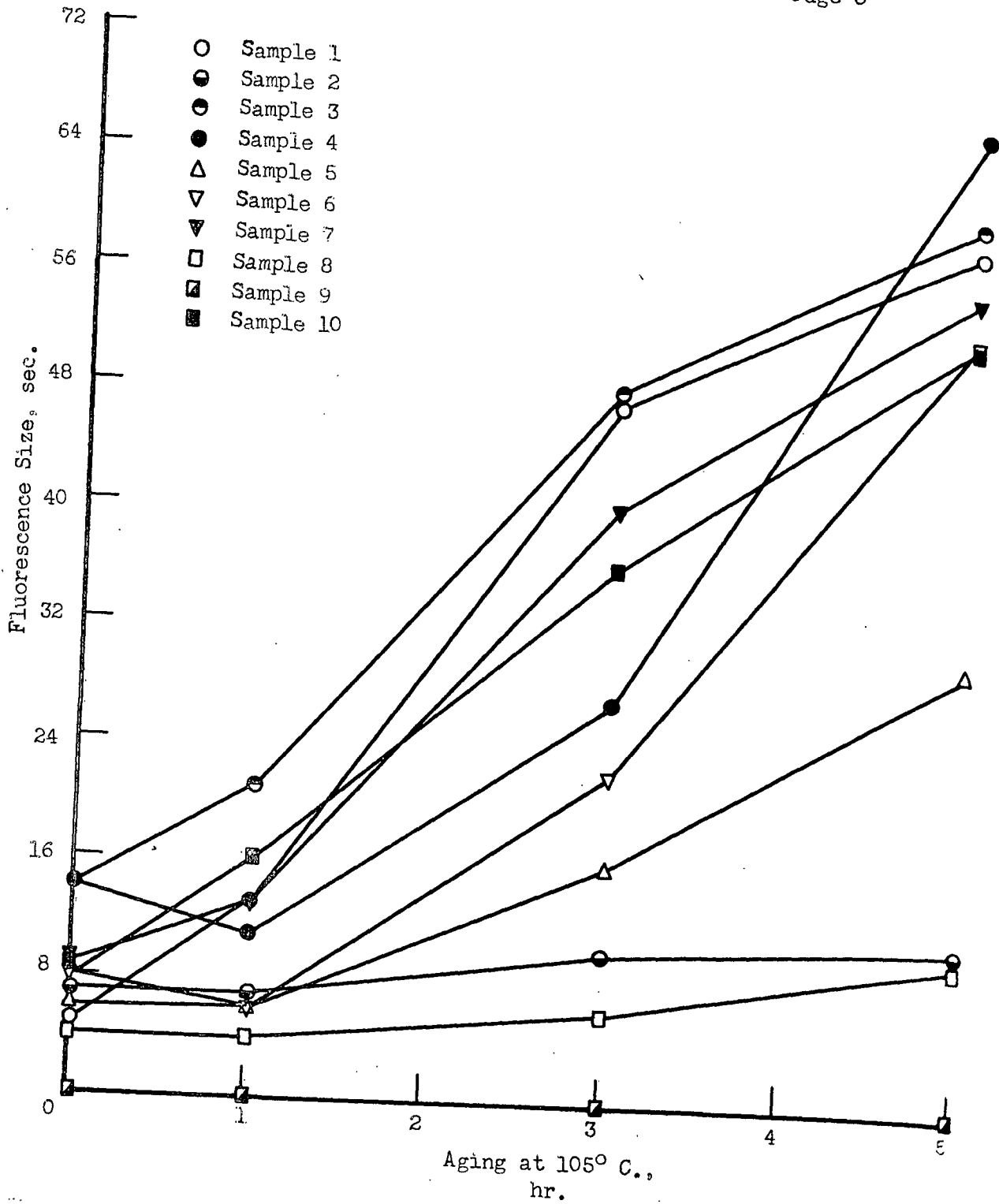


Fig. 1. Fluorescence Size Test vs. Aging Time

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PROJECT NO. 1857
COOPERATOR Institute of Paper Chemistry
REPORT NO. 8
DATE July 22, 1966
NOTE BOOK 1593 and 1831
PAGE 126-160 to 7-107
SIGNED C. Y. Chu
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POSSIBLE METHOD OF INCREASING ABSORBENCY OF WOOD PULP PRODUCTS

FACTORS WHICH AFFECT THE RATE OF SIZING DEVELOPMENT

Part I. Effect of Ions and the Nature of Interaction with Cellulose

SUMMARY

In a continuing study of the factors contributing to the loss of absorbency and the development of self-sizing in paper, a series of experiments was performed in which bleached and unbleached cellophane was treated in three different ways with radioactive stearic acid after "conditioning" the surface with calcium and aluminum ions. The effect of these treatments on the retention of stearic acid was measured.

The results revealed that, with respect to unbleached cellophane, the calcium- and alum-conditioned samples retained more stearic acid than the unconditioned samples. However, the unconditioned samples retained more stearic acid than the ion-treated material when the sample was bleached.

Infrared analysis of the unconditioned and conditioned-bleached cellophane showed an absorption band at 5.74 microns indicative of stretching of ester linkages. The intensity of the absorption appeared to be nearly constant in all but an $\text{NO}_2\text{-CCl}_4$ oxidized unconditioned sample which showed a lower intensity. This latter sample exhibited what appeared to be a weak carboxyl band at 5.86 microns. Unbleached cellophane did not exhibit any type of carbonyl absorption.

EXPERIMENTAL

MATERIALS

Cellophane

The cellophane used was "Visking" cellulose sausage casing manufactured by the Visking Corporation of Chicago. It was decoated by soaking overnight in a tray containing distilled water and then dried under tension prior to use.

Radioactive Stearic Acid

The radioactive stearic acid sample obtained from Volk Radiochemical Company weighed 5.7 mg. and its total activity was 0.1 mc. The stock solution was prepared by dissolving 225 mg. of normal stearic acid and 5.7 mg. C^{14} stearic acid in 50 ml. benzene.

The test solution was prepared as follows: Twenty-five cc. of the stock solution was diluted to a total volume of 50 ml. with purified benzene containing 384.6 mg. of normal stearic acid. This solution contains 2.85 mg. C^{14} stearic acid with 50 μ c. radioactivity and 500 mg. stearic acid. One cubic centimeter of this solution will therefore contain 1 μ c. of radioactivity and 10 mg. stearic acid. In all experiments, the amount of the tagged stearic acid applied or used as the source was 0.0001 g.

PROCEDURES

Bleaching Cellophane Samples

1. By sodium hypochlorite ($NaOCl$)

Decoated cellophane (1.72 g. was bleached in 47.0 g. of 5.25% NaOCl solution at room temperature for about 15 minutes. At the end of this period, the sample was washed with distilled water until it was free of chlorine. The washed sample was mounted on a glass plate to dry.

2. By nitrogen dioxide in carbon tetrachloride ($\text{NO}_2\text{-CCl}_4$) (1)

Nitrogen dioxide gas from a cylinder was bubbled through a glass tubing and a dispersion tube to the bottom of a flask which contained three liters (4740 g.) of carbon tetrachloride. After approximately 10 hours bubbling, 130 g. of nitrogen dioxide were absorbed in the carbon tetrachloride. This mixture was then poured into a desiccator where 16 g. of cut cellophane strips were hung over a glass bar and adjusted in such a way that the cellophane samples were completely immersed in the bleaching mixture. After 45 hours oxidation, the samples were washed in 50% aqueous methanol and dried with acetone and anhydrous ether. The excess ether was removed by vacuum over phosphorous pentoxide over the weekend. (Methanol was used in the washing sequence to stop the oxidation reaction. Methanol reacts instantaneously with nitrogen dioxide as noted by the disappearance of the characteristic brown color of nitrogen dioxide.)

3. By nitrogen dioxide (2)

Decoated cellophane samples (115 g.) were suspended from a glass rod inside a desiccator. Ten grams of gaseous No_2 (Mathieson Co.) was introduced into the desiccator through a glass tubing and a dispersion tube for a total of 125 hours.

Conditioning Cellophane Surfaces for Adsorption

1. With calcium salt--

Bleached and unbleached decoated cellophane was soaked in a mixture of 10^{-4}M CaCl_2 and $2 \times 10^{-4}\text{M}$ KHCO_3 for about one-half to one hour. The conditioned cellophane was dried by securing it to a glass plate with masking tape.

2. With alum--

Decoated cellophane (4.1 g.) was soaked in 820 ml. of water containing 0.164 g. alum. This is equivalent to 4% alum based on the weight of cellophane and the ratio of liquid to cellophane is 1000:5. The samples were soaked for 5 hours and then dried on a glass plate overnight.

Techniques Used for Anchorage of Stearic Acid on Cellophane Film

For the purposes of studying the reaction of salts and stearic acid with cellulose, the anchorage of stearic acid was accomplished by the following three techniques:

1. By immersion--

Air-dried decoated cellophane film was cut to the diameter of a 38 x 200 mm. test tube and dipped into a test solution containing 10 mg. of stearic acid or 1 μ c.radioactivity. The film was then withdrawn and placed diametrically in a test tube to dry. Each tube was placed in a rack fitted in a horizontal position so as to prevent it from rolling. The tubes were heated at 75°C. to remove residual benzene and at the same time to fuse the stearic acid with the cellulose. The tubes were closed with cellophane-covered rubber stoppers and then heated in an oven for 5 hours at 105°C. The radioactivity of the aged samples was measured before and after Soxhlet extraction with benzene. Results obtained for the unbleached samples using this method are summarized in Table I.

2. By surface application or spreading--

One-tenth ml. of tagged stearic acid was spread over a 2 x 2 cm.² area marked in the center of a 4 x 4 cm.² cellophane area. After fusion at 72°C. for 10 minutes, the samples were mounted to the bottom of a culture dish by means of masking tape two layers thick. These samples were aged at 105°C. for different periods (5, 10, and 15 hours). The radioactivity was counted before and after extraction in hot benzene and, in one case, after successive extraction in hot benzene and hot ethanol. The

results obtained for the unconditioned and calcium-conditioned samples (pH 4.3 and 9.5) are shown in Table II.

In a separate experiment, the effect of cold benzene extraction on the stearic acid-treated cellophane samples was also observed. Results are given in Table III.

The surface application technique was also tried on unconditioned and calcium-conditioned NaOCl-bleached cellophane samples. These were aged for 15 hours at 105°C. and successively extracted with cold benzene for 1, 2, and 3 hours. Radioactivity was counted and the results are summarized in Table IV. The same experiment was done on NO₂-CCl₄ bleached samples. Results are shown in Table V.

3. By vapor transport--

Tagged stearic acid (0.01 mg.) was spread over a piece of 2 x 2 cm.² decoated cellophane and laid flat on the bottom of a 60 x 15 mm. culture dish cover. This served as a source of stearic acid. The test cellophane sample was placed next to it but was separated from the stearic acid source by means of a cellophane ring 1 mm. thick. The other portion of the culture dish (bottom dish) was placed so that its bottom covered the test sample. Alum- and calcium-conditioned samples were exposed at different periods. The radioactivity of the exposed at different periods. The radioactivity of the exposed samples was taken and measured again after extraction with benzene. Samples were extracted by immersing them in a

beaker containing the solvent for one hour each time. The results for the unbleached samples are summarized in Table IV. These data are shown graphically in Figures 1 and 2.

The effect of calcium and aluminum ions on $\text{NO}_2\text{-CCl}_4$ bleached cellophane samples using the same procedure are tabulated in Table VII.

Radioactivity Determination

A thin window Geiger tube and a Model 2000 decimal scalar manufactured by the Berkley Scientific Corporation was used to measure radioactivity. The aged specimens were cooled to room temperature, placed on a glass dish, and then under the Geiger tube for counting. Allowing 5% error in the results, the counting time for each sample was determined according to its counting rate (3). The background rate was measured and subtracted from all readings to give the true count.

In all tables, the figures under the column "%" were calculated by dividing the residual radioactivity by the original radioactivity x 100 to give the percentage of chemically combined stearic acid.

Infrared Spectroscopic Examination

The cellophane samples were submitted for infrared examination for the purpose of detecting functional groups. Particular attention was devoted to the detection of carbonyl groups.

The infrared absorption spectra were recorded on a Perkin-Elmer Model 21 recording spectrophotometer. The sample preparation was as follows: A small portion of each sample was hand-ground and mixed with powdered infrared quality potassium bromide. The resulting mixtures were pressed into clear pellets and their infrared absorption spectra recorded.

The unbleached cellophane film was not as hard and brittle as the treated cellophane films, and consequently, could not be hand-ground or mixed with potassium bromide in its original form. This sample was therefore ground in a micro-Wiley mill to pass a 40-mesh screen prior to mixing with potassium bromide. In addition to examining this sample in potassium bromide, a spectrum was also recorded on the original cellophane film. The following five samples were examined by this technique:

- (1) Unbleached cellophane
- (2) $\text{NO}_2\text{-CCl}_4$ bleached cellophane
- (3) $\text{NO}_2\text{-CCl}_4$ bleached cellophane and stearic acid treated
- (4) $\text{NO}_2\text{-CCl}_4$ bleached, calcium and stearic acid treated
- (5) $\text{NO}_2\text{-CCl}_4$ bleached, alum and stearic acid treated

The results are recorded in Table VIII.

EXPERIMENTAL RESULTS AND DISCUSSION

The three bleaching methods gave the following products:

1. NaOCl

The carboxyl content of the cellophane increased from 0.06 to 0.16%.

2. NO_2 (gaseous state)

The resulting sample was very brittle and could not be handled.

The carboxyl content was 0.68%.

3. NO_2 in CCl_4

The samples were also very brittle, but slightly better than the No. 2 samples. After aging, the samples turned dark brown and cracked. The resulting carboxyl contents of the bleached samples were 0.6% to 0.9%.

The three different methods used for anchoring the stearic acid to the cellophane gave the following results.

1. By immersion--

The results in Table I indicated that with higher concentration of acid, the higher was the residual radioactivity after the samples had been aged and extracted in hot benzene; however, the radioactivity did not increase proportionately to each respective concentration. The resulting samples were too rich in acid and it required considerable time for benzene extraction in order to get a constant count on chemically combined acid.

2. By surface application--

By the use of this technique, the average radioactivity in counts per minute (c/m) after fusion for 10 minutes at 72°C. was 5003, 4776, and 4688 for the untreated, and calcium-conditioned at pH 9.5 and at pH 4.3, respectively.

As shown in Table II, in general, the longer the aging time at 105°C., the less acid film left on the cellophane, but the higher the percentage of chemically combined stearic acid. This means that a longer aging time favors this reaction to take place.

The results showed that the calcium-conditioned samples (especially pH 4.3) had a higher percentage of chemically combined stearic acid than the untreated samples. In all cases, the retained stearic acid was completely removed after two extractions in alcohol. In Table III the cold benzene

extracted samples showed slightly higher percentage of chemically combined stearic acid than those extracted in hot benzene. This is probably due to a cleaner solvent and better circulation around the samples in a Soxhlet extractor than when the samples were just immersed in beakers containing the cold solvent.

The effects of calcium ion on the sorption of stearic acid on NaOCl bleached cellophane using the surface application technique are shown in Table IV. For the bleached cellophane, the unconditioned samples retained more stearic acid than the calcium conditioned samples. For the unbleached samples, the calcium-conditioned samples retained more stearic acid than the unconditioned samples.

This might be explained as follows: In the unconditioned bleached samples, ester groups were formed between stearic acid and hydroxyl groups in cellulose (as proved by infrared technique) and $\text{RCOOH} \cdot \text{COOH-R}$ hydrogen bonds might be formed between cellulose and stearic acid. However, in the calcium and alum-treated bleached samples, hydrogen of the carboxyl groups from cellulose is replaced by the ions; hence, the possibility of RCOOH-COOH-R bond formation will be lesser. Therefore, the plain bleached samples would have higher chemically combined stearic acid than the treated bleached samples.

In the case of the unbleached samples, the amount of carboxyl groups was negligible, so that most of the calcium ions remained on the surface unreacted; upon application of stearic acid, calcium stearate may have been trapped in the cellophane even after the sample had been aged and extracted in benzene. This seemingly small amount of calcium or aluminum stearate in addition to the cellulose ester may account for the difference observed.

The effect of residual hypochlorite in the sample was tested by not washing Run 6, but carefully washing Run 5 (Table IV). The results proved that in the presence of excess NaOCl, more stearic acid was retained on the unconditioned cellophane than the calcium-conditioned samples. It may be speculated that with excess bleaching agent more COOH groups were formed in the unconditioned cellophane which reacted with stearic acid or may have formed $\text{RCOOH} \cdot \text{COOH-R}$ hydrogen bonds to give a higher percentage of chemically combined stearic acid. In the case of calcium-conditioned samples, the extra COOH groups coming from the excess bleaching agent may have reacted with the calcium ions before having a chance to react with stearic acid, thus giving a lower count due to the cellulose-ester compound only.

3. By vapor transport--

When the unbleached unconditioned (untreated), calcium-, and alum-conditioned samples were exposed to radioactive stearic acid at 105°C . for different lengths of time,

their radioactivity did not increase proportionately to the time of exposure as shown in Table VI. In general, their respective maximum counts were reached in 20 minutes (Fig. 1). However, as indicated in Fig 2, the calcium- and alum-treated samples again showed higher chemically combined stearic acid than the unconditioned sample. This agreed with the results obtained on unbleached cellophane by the surface application method. This may be attributed to the formation of calcium or aluminum stearate that may be physically trapped on the cellophane surface.

The same results were also observed with the $\text{NO}_2\text{-CCl}_4$ bleached samples as shown in Table VII. The unconditioned $\text{NO}_2\text{-CCl}_4$ bleached samples retained more stearic acid than the conditioned samples.

By comparison of some data gathered from Tables II-VII, the sorption of stearic acid increased when the carboxyl content increased by the surface application technique. For the vapor transport method, the unbleached samples were extracted only twice in benzene instead of three times, so no such comparison can be made.

Infrared Analysis

The infrared analysis of the five different samples are shown in Table VIII.

The first four samples listed all exhibit absorption at or near 5.74 microns. Absorption at this wavelength has been assigned to the C=O stretching of ester groups by O'Connor (4). The C=O stretching of acids according to O'Connor occurs at 5.85 microns. An earlier investigation by Forziati and co-workers (5) on the determination of carboxyl groups in cellulose assigned absorption at 5.80 to the C=O stretching of acids.

In addition to the above correlations associated with cellulose products, the following absorption limits in this region have been established by Bellamy (6). This is only a partial listing.

<u>C=O Stretching Vibration</u>	<u>Wavelength, microns</u>
Saturated open-chain ketones	5.70 - 5.87
$\alpha\beta$ -unsaturated ketones	5.93 - 6.01
Saturated aliphatic aldehydes	5.75 - 5.82
$\alpha\beta$ -unsaturated aldehydes	5.87 - 5.96
Normal saturated esters	5.72 - 5.77
$\alpha\beta$ -unsaturated and arylesters	5.78 - 5.83
Saturated aliphatic acids	5.80 - 5.89
$\alpha\beta$ -unsaturated acids	5.84 - 5.92

The 5.74-micron absorption band of the cellophane samples therefore appears to be associated with ester carbonyl groups rather than carboxyl groups.

The rather detailed comparison of ester carbonyl to carboxyl absorption was undertaken because of the stearic acid treatment given to a number of these samples. The carboxyl absorption of stearic acid, as determined previously, occurs at 5.86 microns.

The small absorption, mentioned previously, at 5.86 microns in the spectrum of $\text{NO}_2\text{-CCl}_4$ bleached sample occurs within the area of saturated aliphatic acid absorption.

The spectrum of unbleached cellophane is devoid of any type of carbonyl absorption. This is evident in the spectrum from the potassium bromide disk technique and also in the very strongly absorbing cellophane film.

The infrared examination of the cellophane samples was originally intended to be a qualitative study. As a consequence, no effort was made to maintain either a constant or known sample concentration. However, it is evident that $\text{NO}_2\text{-CCl}_4$ bleached sample contains a smaller quantity of carbonyl groups than the remaining samples. The intensity of carbonyl absorption in the remaining treated cellophane samples appears to be nearly equal.

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TABLE I

THE EFFECT OF TAGGED STEARIC ACID CONCENTRATION ON THE RESIDUAL
 RADIOACTIVITY OF UNBLEACHED CELLOPHANE
 (IMMERSION TECHNIQUE)

Treatment	Stearic Acid Concentration, $\mu\text{c/ml}$					
	1		0.5		0.2	
	c/m ^a	%	c/m ^a	%	c/m ^a	%
Aged at 105°C. for 5 hrs.	Max.	286	85		53	
	Min.	147	44		25	
	Av.	208	67	100	35	100
Extracted in hot benzene for two hours	Max.	235	62		62	
	Min.	93	29		29	
	Av.	147	44	65.6	44	
Extracted in hot benzene for three hours	Max.	228	73		38	
	Min.	141	35		10	
	Av.	172	53	79.1	26	74.3

Note: Each figure given is the average of eight determinations.

(a) Counts per minute

TABLE II

EFFECT OF CALCIUM ION AND AGING ON THE SORPTION OF
STEARIC ACID ON UNELEACHED CELLOPHANE

(Surface Application Technique)

Treatment	Aging, time, hrs.											
	Five				Ten				Fifteen			
	Uncondi- tioned	Condi- tioned	Ca pH 9.5	Condi- tioned	Uncondi- tioned	Condi- tioned	Ca pH 9.5	Condi- tioned	Uncondi- tioned	Condi- tioned	Ca pH 9.5	Condi- tioned
	Cellophane c/m %	Cellophane c/m %	c/m %	Cellophane c/m %	Cellophane c/m %	Cellophane c/m %	c/m %	Cellophane c/m %	Cellophane c/m %	Cellophane c/m %	c/m %	Cellophane c/m %
Aged at 105°C												
Max.	3433	4671	2788	2151	2868	1249	2002	2917	1896			
Min.	3112	2283	2178	1475	2473	694	1001	1270	988			
Av.	3314	3546	2562	1706	2679	921	1610	1843	1302			
Extracted in hot benzene for one hour												
Max.	94	104	81	92	93	100	94	111	101			
Min.	57	82	58	53	86	83	63	73	79			
Av.	72	95	68	72	89	92	80	93	91			
Extracted in hot benzene for two hours												
Max.	67	96	88	72	91	83	70	87	73			
Min.	38	71	59	37	74	66	37	49	55			
Av.	53	82	73	60	83	76	57	72	64			
Extracted in hot benzene for three hours												
Max.	79	86	69	72	77	76	72	85	77			
Min.	52	79	52	41	61	52	47	62	53			
Av.	68	82	61	60	69	65	61	73	64			
Extracted in hot ethanol for one hour												
Max.	21	20	26	29	31	29	37	50	37			
Min.	9	18	21	20	17	20	20	26	24			
Av.	16	19	23	23	25	24	30	40	32			
Extracted in hot ethanol for two hours												
Max.	12	10	16	15	22	23	27	20	23			
Min.	7	6	11	11	17	14	11	15	20			
Av.	10	9	14	12	20	18	16	17	22			

TABLE III

EFFECT OF CALCIUM ION AND AGING ON
 THE SORPTION OF STEARIC ACID ON UNBLEACHED CELLOPHANE
 (Surface Application Technique)

Treatment		Unconditioned				Calcium Conditioned (pH 9.5)			
		Run 1		Run 2		Run 1		Run 2	
		c/m ^a	%	c/m ^a	%	c/m ^a	%	c/m ^a	%
Fused at 72°C. for 10 min.	Max.	5515		6341		5424		5383	
	Min.	4910		5631		4799		4874	
	Av.	5130		6024		5143		5090	
Aged at 105°C. for 15 hrs.	Max.	2524		3726		1881		3367	
	Min.	2176		3030		1040		2253	
	Av.	2375	100	3383	100	1487	100	2668	
Extracted in c cold benzene for one hr.	Max.	141		148		135		145	
	Min.	95		108		129		122	
	Av.	112	4.7	131	3.9	132	8.9	132	4.9
Extracted in cold benzene for two hrs.	Max.	117		141		125		138	
	Min.	96		105		104		107	
	Av.	105	4.4	124	3.7	114	7.7	120	4.5
Extracted in col cold benzene for three hrs.	Max.	112		123		127		121	
	Min.	96		99		109		89	
	Av.	102	4.3	113	3.3	116	7.8	109	4.1

(a) Counts per minute

Note: Each figure given above is the average of three determinations.

TABLE IV
EFFECT OF CALCIUM ION AND AGING ON THE SORPTION OF STEARIC ACID
ON NaOCl-BLEACHED CELLOPHANE
(Surface Application Technique)

Treatment	unconditional cellophane						calcium conditioned cellophane					
	Run 1 c/m	Run 2 c/m	Run 3 c/m	Run 4 c/m	Run 5 ^a c/m	Run 6 ^b c/m	Run 1 c/m	Run 2 c/m	Run 3 c/m	Run 4 c/m	Run 5 ^a c/m	Run 6 ^b c/m
Fused at 72°C. for 10 min.	Max. 4986	5066	6007	5169	5517	6242	5961	5965	5225	4991	5465	5835
Min.	4986	3917	5382	4889	5050	5539	4879	5356	4710	4463	4717	4676
Av.	5068	4622	5592	5045	5217	5971	5437	5611	5031	4681	5036	5241
Aged at 105°C. for 15 hours	Max. 4051	3346	5110	3534	1867	5400	4261	3475	2312	3390	4621	4609
Min.	3018	2097	4259	2946	1103	4482	3573	3110	2123	1896	3617	3751
Av.	3578	2846	4603	3022	1399	5004	3826	3325	2240	2769	3989	4094
Extracted in cold benzene for one hour	Max. 531	185	632	595	112	1800	590	143	146	142	126	198
Min.	482	98	343	312	99	1393	222	104	126	96	98	166
Av.	512	14.3	479	443	106	1530	411	129	135	122	110	180
Extracted in cold benzene for two hours	Max. 444	164	155	472	98	1463	470	119	137	116	107	128
Min.	408	116	111	256	93	1030	187	101	127	103	92	105
Av.	431	12.0	134	347	95	1213	333	112	130	109	100	113
Extracted in cold benzene for three hrs.	Max. 432	120	128	432	110	1188	453	102	114	105	151	145
Min.	358	84	108	312	85	817	165	87	106	104	104	112
Av.	406	11.3	120	406	100	955	308	96	110	132	132	127

(a) These two samples were carefully washed after bleaching.

(b) These two samples were purposely not washed enough after bleaching.

Note: Each figure given above is the average of three determinations.

TABLE V
 EFFECT OF IONS AND AGING ON NO₂-CCl₄ BLEACHED CELLOPHANE
 ON THE SORPTION OF STEARIC ACID
 (Surface Application Technique)

Treatment		Unconditioned		Calcium Conditioned		Alum conditioned	
		c/m ^a	%	c/m ^a	%	c/m ^a	%
Aged at 105°C. for 15 hours	Max.	1237		1312		682	
	Min.	597		764		398	
	Av.	830	100	1027	100	566	100
Extracted in cold benzene for one hour	Max.	140		91		80	
	Min.	110		63		63	
	Av.	121	14.6	74	7.2	71	12.5
Extracted in cold benzene for two hours	Max.	131		80		84	
	Min.	83		65		71	
	Av.	114	13.7	74	7.2	78	13.8
Extracted in cold benzene for three hours	Max.	136		70		76	
	Min.	84		62		61	
	Av.	108	13.0	67	6.5	70	12.4

a Counts per minute

Note: Each figure given above is the average of four determinations.

TABLE VI

Treatment	Exposure, Time, Minutes															
	Five				Ten				Fifteen				Twenty			
	Uncon- ditioned	Alum	Calcium	Conditioned	Uncon- ditioned	Alum	Calcium	Conditioned	Uncon- ditioned	Alum	Calcium	Conditioned	Uncon- ditioned	Alum	Calcium	Conditioned
	c/m	%	c/m	%	c/m	%	c/m	%	c/m	%	c/m	%	c/m	%	c/m	%
Exposed to acid source	Max.	236	309	319	378	343	409	395	393	412	510	484	437			
	Min.	177	149	106	178	230	206	234	241	226	129	239	242			
	Av.	212	100	238	100	285	100	285	306	302	100	249	100	364	100	331
Extracted in cold benzene for one hour	Max.	10	16	13	12	27	34	23	26.0	22	29	21	17			
	Min.	0	4	0	0	0	12	4	5.0	2	2	2	0			
	Av.	4	1.9	10	4.2	5	2.5	23	12	16.5	11	6.4	10	2.7	10	3.0
Extracted in cold benzene for two hours	Max.	10	29	21	14.0	22	23.0	16	15	20	51	27	29			
	Min.	4	4	4	6.0	8	14.0	0	1	3	8	4	9			
	Av.	8	3.8	9.2	10.5	15	5.3	15.6	10	13	15.6	13	13	3.6	13	3.9

TABLE VII

EFFECT OF IONS ON THE SORPTION OF
 STEARIC ACID, K_2CO_3 -CCl₄ ETCHED CELLOPHANE

(Vapor Transport Technique)

Treatment		Unconditioned ^c		Calcium conditioned ^c		Alum conditioned ^c	
		c/m ^a	%	c/m ^a	%	c/m ^a	%
Exposed to the acid source at 105°C. for 10 min.	Max.	720		637		551	
	Min.	277		371		302	
	Av.	481	100	479	100	408	100
Extracted in cold benzene for one hour	Max.	44		28		36	
	Min.	23		6		6	
	Av.	36	7.5	16	3.3	18	4.4
Extracted in cold benzene for two hours	Max.	51					
	Min.	14					
	Av.	28	5.8				
Extracted in cold benzene for three hours	Max.	31		15		17	
	Min.	19		6		8	
	Av.	26	5.4	12	2.5	12	2.9

(a) Counts per minute

(b) Each figure is the average of six determinations.

(c) Each figure is the average of four determinations.

TABLE VIII
 ABSORPTION BANDS OF CELLOPHANE SAMPLES
 (wavelength in microns)

Sample*					Possible Interpretation
1	2	3	4	5	
2.94	2.95	2.93	2.94	2.95	O-H stretching
3.47	3.48	3.47	3.48	3.47	C-H stretching (non-aromatic)
5.74	5.75	5.74	5.74	----	C=O stretching (ester)
----	----	----	5.86	----	C=O stretching (acid)
6.10	6.10	6.10	6.11	6.12	absorbed H ₂ O, and/or C=C stretching non-conjugated
7.30	7.30	7.30	7.30	7.28	C-H deformation, characteristic of cellulose
7.81	7.81	7.81	7.81	----	O-H deformation, and/or CH ₂ wagging, characteristic of cellulose
8.16	8.16	8.15	8.14	8.15	O-H deformation, and/or CH ₂ wagging, characteristic of cellulose
9-10	9-10	9-10	9-10	9-10	Cellulose ring
11.20	11.20	11.20	11.20	11.20	CH ₂ wagging, Measure of degree of crystallinity

*The samples are identified as follows:

1. NO₂-CCl₄-p NO₂-CCl₄ bleached, stearic acid treated
2. 1857-1831-103-Ca NO₂-CCl₄ bleached, stearic acid & calcium conditioned
3. 1857-1831-103-Al NO₂-CCl₄ bleached, stearic acid & aluminum conditioned
4. 1857-1831-58 -O NO₂-CCl₄ bleached
5. Unbleached cellophane

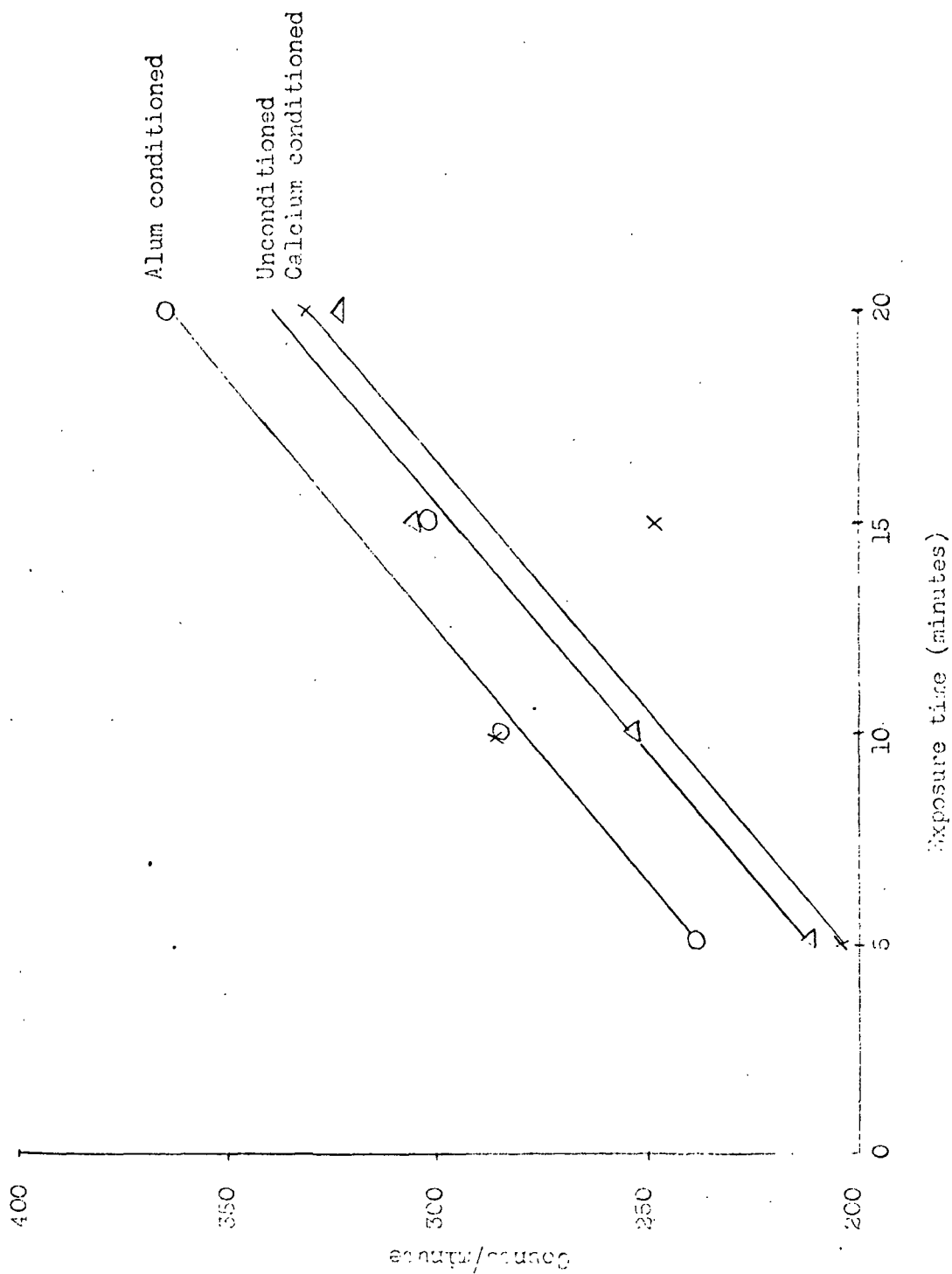


Fig. 1 Effect of ions and aging on the sorption of stearic acid on unbleached cellophane by the vapor transport method.

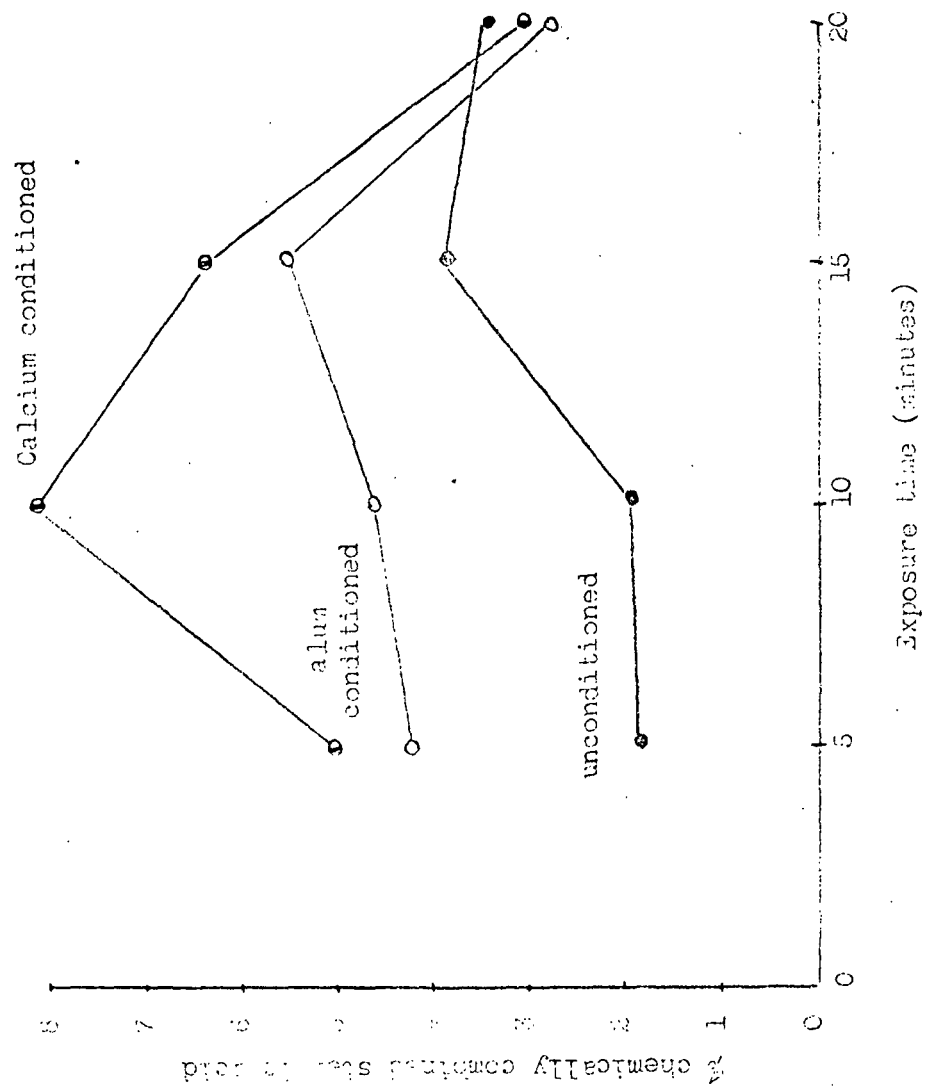


Fig. 2 Effect of exposure time (vapor transport method) on % chemically combined stearic acid

POSSIBLE METHOD OF INCREASING ABSORBENCY OF WOOD PULP PRODUCTS

FACTORS WHICH AFFECT SIZING DEVELOPMENT

Part II. Effect of Moisture Content on Sizing Development in Handsheets Prepared From Solvent- Extracted Pulp

SUMMARY

One of the factors that may greatly affect sizing development in paper is water (moisture). This investigation, as a part of a continuing study on self-sizing of paper, was conducted to determine the effect of moisture at certain temperatures. Handsheets, prepared from benzene-alcohol-extracted unbleached Mitscherlich pulp, were treated with stearic acid; conditioned to several moisture contents (8.4, 3.1, and 0.5%), and aged at 75°C. Results showed that for the first 26 to 30 hours aging, sizing increased rapidly for the 8.4% moisture sample, but after this period, the lower moisture samples (3.1 and 0.5%) were sized faster. However, when another set of these handsheets were aged at lower temperatures (50 and 25°C.), it was noted that the higher the moisture content of the sample, the more rapid was the sizing development. In the next series of experiments, the moisture content of the sheets was controlled so that the samples at a given humidity level retained approximately the same amount of moisture regardless of the temperature used. The results showed that the rate of sizing was always faster for the higher temperature samples in the same moisture level. On the other hand, comparison of the samples of the different moisture levels at the same temperature (75°C.), showed that the rate of sizing development was faster for the lower R.H. samples, whereas for those aged at lower temperatures (50 and 25°C.), sizing was faster for the higher R.H. samples.

In general, the higher temperature was more effective in developing sizing at lower humidities whereas the lower temperatures were more effective at higher humidities. Hence, there must be optimum conditions of temperature and moisture to favor sizing development.

INTRODUCTION

It is noted in the literature that the influence of moisture content in paper and in the properties of finished products is a very important one. Casey (1) mentioned that a certain amount of water (moisture) is desirable in all paper, either for internal sizing or surface sizing. Czepiel (2) found that the maximum color reversion occurred at moisture contents of around 5% for cotton linters. Kaustinen and Jappe (3) have reported that much higher brightness reversion occurred in higher equilibrium moisture contents than in the P_2O_5 dried handsheets.

The above results may also have an important bearing on self-sizing problems of paper and wood pulp products. Therefore, the object of this study is to determine the effect of moisture in the sizing development of handsheets prepared from solvent-extracted pulp.

EXPERIMENTAL PROCEDURES

PREPARATION OF BENZENE-ALCOHOL-EXTRACTED PULP

A 400-gram unbleached, air dried, Mitscherlich sulfite pulp sample was extracted for 24 hours in a large Soxhlet with eight liters of a 2:1 benzene-alcohol mixture. The pulp was then air dried and stored in a large bottle for future use.

PREPARATION OF HANDSHEETS

The 400-gram extracted pulp sample was soaked in six liters of deionized water overnight and then beaten in a Valley beater at a consistency of 1.5% to a Schopper-Riegler freeness of 720 cc.

The pulp suspension was diluted to a 0.5% consistency and sheets (60-lb.--25x40/500 basis wt.) were prepared in the Valley sheet mold, pressed at 50 lb./in.² for five minutes, and dried on a steam drier with 4 lb. steam pressure for seven minutes. The dried handsheets were placed immediately in a polyethylene bag to prevent exposure to air.

PRELIMINARY TESTS

Preliminary experiments were conducted to establish the proper amount of stearic acid to be applied to provide reasonable size values. Several concentrations of stearic acid, ranging from 0.02-0.40% based on the weight of the pulp were applied on both sides of an 0.8-g. extracted sheet. As soon as the benzene was evaporated, the stearic acid was redistributed by spraying benzene solution on both sides of the sheet. Each sheet was fused in an oven

at 75°C. for one hour. Size values were determined by the flotation test and by a water drop method. Results are recorded in Table I.

A second series was run to compare size values of dry and 88.4% R.H. conditioned sheets treated with 0.1, 0.2, and 0.4% stearic acid. These samples were aged at 103°C. for 1/2 to 6 hours. Size values were determined by the flotation method. Results are summarized in Table II and graphically shown in Figure 1.

SIZING OF BENZENE-EXTRACTED SHEETS WITH 0.2% STEARIC ACID

Based on the preliminary tests, 0.2% of stearic acid (based on fiber) was selected as the level to use in subsequent experiments. This amount of stearic acid in benzene solution was applied on both sides of an 8 by 8-inch extracted sheet. As soon as the benzene was evaporated from the sheet, the stearic acid was redistributed by spraying benzene on both sides. These samples were then suspended and fused separately in an oven at 80°C. for one hour.

CONDITIONING OF TEST SAMPLES IN CaCl_2 DESSICATOR UNDER VACUUM

After fusion 24 of these sized sheets were stacked in one pile and cut into 1-3/4 by 1-1/4-inch size, with a hole punched at one end of each pile and clamped together with a paper clip. These cut samples were preconditioned in a CaCl_2 desiccator for at least 24 hours under vacuum. They were then ready for aging.

PREPARATION OF H_2SO_4 SOLUTIONS FOR VARIOUS AGING HUMIDITIES (4)

Nine concentrations of sulfuric acid were prepared by diluting the concentrated acid with distilled water to the approximate concentration. The strengths were checked for specific concentration both by hydrometer and by titration with standard NaOH solution.

The following concentrations were selected;

64.8, 66.6, and 68.3% for providing 10% R.H.

50.9, 52.5, and 54.0% for providing 35% R.H.
for

30.4, 31.4, and 32.4% providing 75% R.H.

AGING THE SIZED SAMPLES AT DIFFERENT HUMIDITIES

A 500-cc. portion of the prepared H_2SO_4 was poured into an eight-inch diameter vacuum desiccator and was warmed to the desired temperature one day in advance to assure the right humidity in the enclosed space when the test samples were put in. In each desiccator, a metal bar with ten hooks was placed across the top, and the test sample (usually composed of five 1-3/4 by 1-1/4-inch sheets representing five samples from five different handsheets) was suspended from a hook. The desiccator with the samples was then placed in an oven set at the desired temperature. When the first aging time was reached, one group of the test samples was removed for the sizing test, and the remainder left for further aging. The results of aging the samples at different humidities and temperatures are shown in Tables III to VIII and graphically shown in Figures 2 to 7.

Determination of Moisture Content of Test Sample at a Specified Humidity

Approximately two grams of the sized and preconditioned samples were weighed for moisture content determination. The samples were placed in weighing bottles and kept at a specified humidity for at least 24 hours, or until such time that two weighings were more or less constant. After drying in an oven, the bottles with the covers on were conditioned for 30 minutes in a 50% R.H. room before weighing. The moisture content was calculated and based on the CaCl_2 preconditioned weight.

Determination of Sizing Developed by Aging

A test sample (a group of five) from the 10 or 35% R.H. aging were suspended from a line in the 50% R.H. room for 30 minutes before the size test was made. If the sample was aged in 75% R.H., it was dried in concentrated H_2SO_4 desiccator under vacuum for 30 minutes and then put in a 50% R.H. atmosphere for another 30 minutes before the size test was made.

To avoid contamination of samples incurred in the process of transferring from one desiccator to another, a specimen $1-1/4$ by $1-1/4$ -inch in size was cut from the $1-3/4$ by $1-1/4$ -inch sample. This piece was used for the size test by floating it on water kept in a 50% R.H. room. The uniformity of stearic acid on the sheet was observed and the time in seconds, for water to penetrate the whole surface was recorded.

RESULTS AND DISCUSSION

Before extensive experiments were carried out, preliminary experiments had to be run to determine what amount of size should be applied to a benzene-extracted sheet in order to obtain reasonable size times during aging. For the first experiment, results in Table I showed that 0.2% concentration developed reasonable lengths of time (size times) during aging as measured by the flotation and water drop tests.

The second experiment was the same as the first one except that the samples were aged at a dry condition and at 88.4% relative humidity. The results are shown in Table II and graphically shown in Figure 1. In many cases, the beginning of the sorption process showed a slight decrease in sizing. This may be due to the loss of sizing agent by evaporation. It is also indicative of a strong association between cellulose and water. Of the several acid concentrations tried, 0.1 and 0.2% gave moderate size times.

Using known data on the external surface of one gram unbeaten pulp and the size of stearic acid molecules, computations showed that 0.2% stearic acid (based on 2.7 g. extracted sheet) will be sufficient to cover the external surface of the fibers in the sheet.

From the above results, a 0.2% stearic acid was therefore, used in this study.

The effect of moisture controlled aging at 75°C. on the rate of sizing is shown in Table III and Figure 2. It was observed that there was a rapid increase of sizing for the higher moisture sample (8.4%) but only

up to about 26 to 28 hours aging. After this period, the rate of sizing was faster for the 3.1% moisture with a size value of 158 sec. at 28 hours aging, compared to 43.7 and 108 sec. for the 0.5 and 8.4% moisture samples, respectively.

The effect of moisture at lower temperatures was observed at 50 and 25°C. Here the samples aged at higher moisture content became sized faster than the lower moisture samples as shown by the data in Table IV and Fig. 3 and 4.

Although moisture was controlled in this series of experiments, the size values obtained are not comparable for the three temperatures, because moisture absorbed by the sheets varied for each temperature. For example, at 75°C. and at 75% R.H., the sheet moisture contents for the 75, 50, and 25°C. were 8.4, 3.5, and 9.5%, respectively. Hence, another set had to be performed.

In this series of experiments, the moisture content was controlled so that the samples at the same humidity level had adsorbed more or less the same moisture at the different temperatures used: 0.50-0.99% for the 10% R.H.; 3.1-4.9% for the 35% R.H.; and 8.4-9.5% for the 75% R.H. All three sets of samples were subjected to three different temperatures at 25, 50, and 75°C., respectively. As shown by the data in Tables V, VI, and VII and Figures 5, 6, and 7, the rate of sizing was always faster for the higher temperature samples in the same relative humidity group. However, samples at the same temperature (specifically, at 75°C.), but at different relative humidity atmosphere, showed quicker rate of sizing for the lower R.H. samples. At lower temperatures (50 and 25°C.) it was the reverse; the higher R. H. samples showed more rapid development.

In general, the higher temperature was more effective in sizing at lower humidities whereas lower temperatures were effective at higher humidities. Hence, there must be optimum conditions of temperature and moisture to favor sizing development. The observed phenomenon appears to be the result of the combined effects of having the right amount of moisture to pick up sizing and the thermal effect which breaks the cellulose-cellulose hydrogen bonds to free a greater number of OH- groups for sorption.

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TABLE I

CORRELATION OF AMOUNT OF SIZE APPLIED TO BENZENE
EXTRACTED SHEET AND RESULTING SIZE TEST

Size Applied, %	Sizing Test, sec. ^a	
	Flotation Method	Water Drop Test ^b
0.00	6.8	140.9
0.02	11.5	264.2
0.04	12.1	286.0
0.08	24.2	677.4
0.10	9.8	181.2
0.15	15.4	136.3
0.20	24.5	310.7
0.40	34.2	143.7

^aAverage of two determinations

^bThis test consisted of adding a small drop of distilled water to the sheet from a height of one inch, using a Black & Decker 5-cc. hypodermic syringe and a Black & Decker No. 25 Yale S.S. needle.

THE EFFECT OF MOISTURE AND AGING AT 103°C. ON SIZING

Amt. Stearic Acid Applied and Aging Humidity		Aging Time, hr.	Size Test, seconds	Av.
0.0%,	Dry	0	6.5, 10.2, 6.8, 13.6	9.3
		1/2	5.0, 8.9, 9.3, 8.8	8.0
		1	7.1 8.2, 7.4, 10.9	8.4
		2	11.1, 10.6, 9.9, 8.6	10.1
		4	8.9, 8.2, 13.1, 7.4	9.4
		6	9.5, 13.6, 9.7, -	10.9
0.0%,	88.4% humidity	1/2	5.2, 7.7, 7.6, -	6.8
		1	5.1, 6.2, 5.8, 7.2	6.1
		2	6.1, 7.6, 7.1, 8.9	7.4
		4	5.0, 17.8, 10.9, 15.1	12.2
		6	7.9, 10.6, - -	9.2
0.1%,	Dry	0	21.0, 19.3, 22.5, 19.2	20.5
		1/2	17.1, 16.6, 17.8, 14.5	16.5
		1	15.1, 23.1, 24.3, 19.2	20.4
		2	18.0, 22.0, 20.6, 15.1	18.9
		4	16.9, 17.1, 17.5, 16.3	17.0
		6	19.0, 22.1, 19.3, 19.8	20.0
0.1%,	88.4% humidity	1/2	19.8, 17.1, 18.7, 17.7	18.3
		1	19.8, 19.0, 14.6, 15.1	17.1
		2	16.8, 18.1, 15.7, -	16.9
		4	25.3, 25.4, 23.1, 26.9	25.2
		6	39.9, 48.3, 59.1, 45.8	48.3
0.2%,	Dry	0	17.3, 22.1, 19.2, 16.5	18.8
		1/2	18.7, 15.3, 23.2, 17.9	18.8
		1	17.9, 14.8, 20.2, 13.0	16.5
		2	16.4 24.0 15.8, 14.3	17.6
		4	15.9, 15.2, 21.1, 14.7	16.7
		6	23.2, 24.0, 28.1, 20.5	24.0
0.2%,	88.4% humidity	1/2	18.1, 19.1, 22.8, 20.9	20.2
		1	17.9, 17.6, 15.1, 11.9	15.6
		2	26.7, 20.3, 24.5, 21.7	23.3
		4	32.4, 29.5, 32.0, 27.7	30.4
		6	47.5, 52.5, 49.6, -	49.9
0.4%,	Dry	0	18.8, 19.5, 13.4, 10.9	15.6
		1/2	13.5, 18.1, 15.7, 12.3	14.9
		1	13.4, 16.1, 11.3, 11.8	13.2
		2	11.7, 17.5, 14.2, 12.1	13.9
		4	12.9, 21.6, 21.5, 12.9	17.2
		6	82.0, 91.7, 104, 35.6	78.4
0.4%,	88.4% humidity	1/2	20.1, 23.2, 17.5, 16.8	19.4
		1	14.5, 15.9, 12.7, 13.5	14.2
		2	19.0, 20.6, 22.5, 17.8	20.0
		4	109, 95.6, 91.5, 69.3	91.3
		6	95.6 118 103 139	114.0

○—○ 0.0% stearic acid, dry
●—● " " " , 68.4% R.H.
△—△ 0.1% " " , dry
▲—▲ " " " , 68.4% R.H.

○—○ 0.2% stearic acid, dry
●—● " " " , 68.4% R.H.
□—□ 0.4% " " , dry
■—■ " " " , 68.4% R.H.

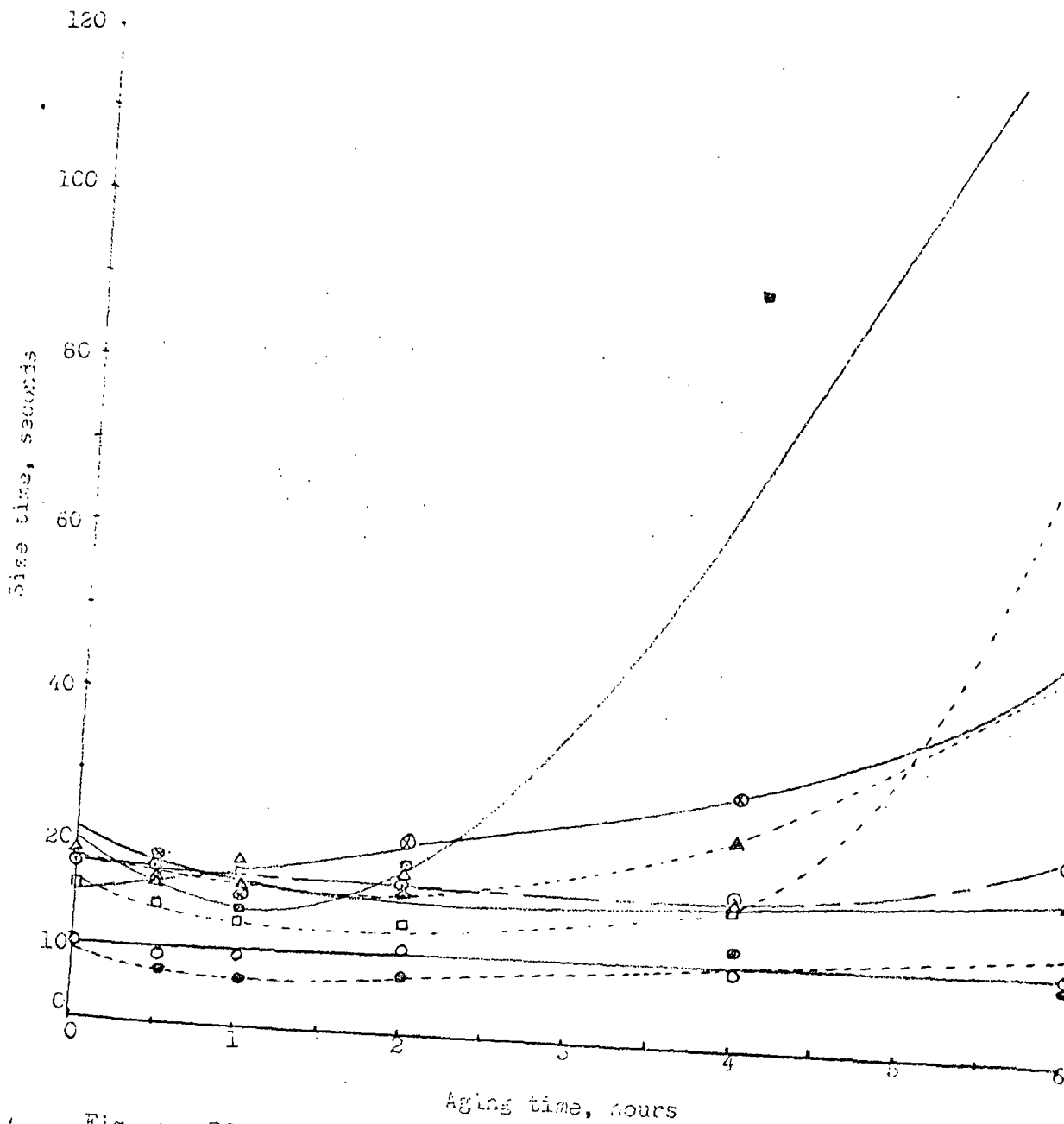


Fig. 1 Effect of moisture and aging at 103°C on the rate of sizing development

TABLE III

RATE OF SIZING AT MOISTURE CONTROLLED AGING AT 75°C.

Aging Time, hr.	Size Test, sec.					Av.
Moisture Content, 0.50%						
0 (control)	20.6					
8	17.5, 19.9, 17.9, 17.1, 18.3					18.1
16	17.3, 17.5, 20.0, 19.6, 20.8					19.1
20	21.4, 23.9, 25.6, 19.6, 17.5					21.6
24	22.8, 24.0, 21.8, 17.8, 18.2					20.9
28	48.3, 72.1, 37.0, 33.4, 27.7					43.7
36	300+, 300+, 300+, 300+, 300+					300+
Moisture Content, 3.1%						
0 (control)	20.6					
8	14.5, 16.6, 14.9, 16.6, 14.1					15.3
16	29.8, 21.8, 22.9, 20.6, 21.2					23.3
20	27.0, 26.0, 33.6, 23.7, --					27.6
24	31.5, 31.3, 29.0, 30.3, 29.1					30.2
28	84.0, 14.1, 65.2, 203, 300+					159
Moisture Content, 8.4%						
0 (control)	20.6					
8	56.5, 33.0, 31.7, 26.5, 17.0					33.0
16	42.5, 42.9, 37.2, 43.7, 30.9					39.4
20	51.2, 62.3, 54.1, 40.6, 46.5					50.9
24	36.6, 39.3, 47.5, 41.4, 38.9					40.7
28	136, 75.1, 91.0, 75.6, 164					108
36	65.0, 57.0, 100, 74.0					74
40	97.1, 128, 123, 132, 151					136
44	55.3, 131, 141, 83.0, 167					115
52	300+, 300+, 300+, 225, 300+					300+

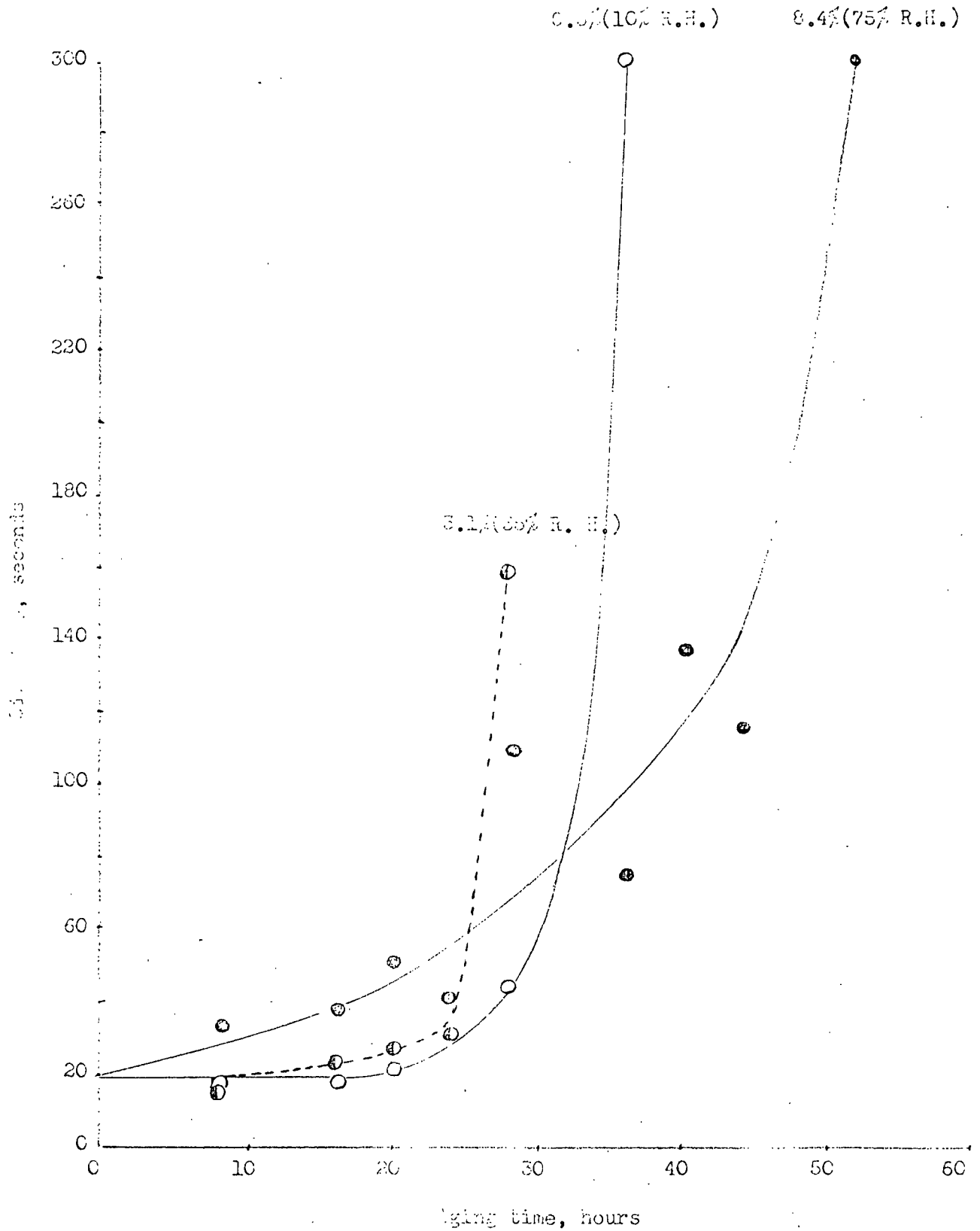


Fig. 2 Effect of moisture controlled aging (75°C) on the rate of sizing development

TABLE IV

RATE OF SIZING AT MOISTURE CONTROLLED AGING AT 90%

Aging
Time,
hr.

Size Test, sec.

Moisture Content, 0.80%

Control	23.0
24	21.7, 13.1, 14.8, 10.4, 24.0
48	32.1, 22.0, 21.5, 12.2, 18.1
96	19.2, 21.7, 23.5, 10.9, 12.8
168	24.4, 20.5, 11.2, 11.3, -
192	21.2, 21.3, 17.6, 22.5, 8.4
264	16.9, 13.6, 20.2, 12.9, 31.0
336	13.3, 30.8, 32.7, 33.4, 21.5
408	22.4, 27.6, 28.4, 31.9, 29.0
456	28.4, 23.6, 26.6, 34.5, 24.2
528	47.7, 300+, 135, 38.4, 88.5
540	130, 300+, 300+, 300+, 67.1

Moisture Content, 3.8%

Control	29.2
25	12.1, 14.3, 15.4, 13.1, 14.5
48	25.9, 25.8, 17.7, 15.2, 15.7
120	12.5, 26.9, 30.2, 22.8, 13.3
144	12.6, 17.1, 16.3, 13.9, 19.8
168	11.2, 13.2, 13.7, 12.6, 25.8
216	20.4, 14.2, 10.0, 13.8, 21.4
312	13.3, 36.1, 27.3, 30.8, 42.6
336	25.8, 23.3, 30.8, 21.5, 58.0
384	300+, 24.1, 300+, 300+, 38.4

Moisture Content, 8.5%

Control	26.2
24	12.8, 12.6, 22.0, 22.8, 19.5
48	14.6, 35.4, 12.5, 17.2, -
54	11.3, 16.8, 20.2, 12.6, 15.7
71	47.2, 22.9, 16.6, 30.2, 43.0
78	30.3, 12.1, 12.1, 26.9, 25.5
120	18.7, 17.8, 46.5, 51.3, 18.9
168	29.5, 24.9, 34.1, 50.3, -
192	26.9, 43.3, 23.4, 40.9, 55.6
240	123, 110, 140, 125, 300+
246	54.8, 300+, 126, 31.5, 300+

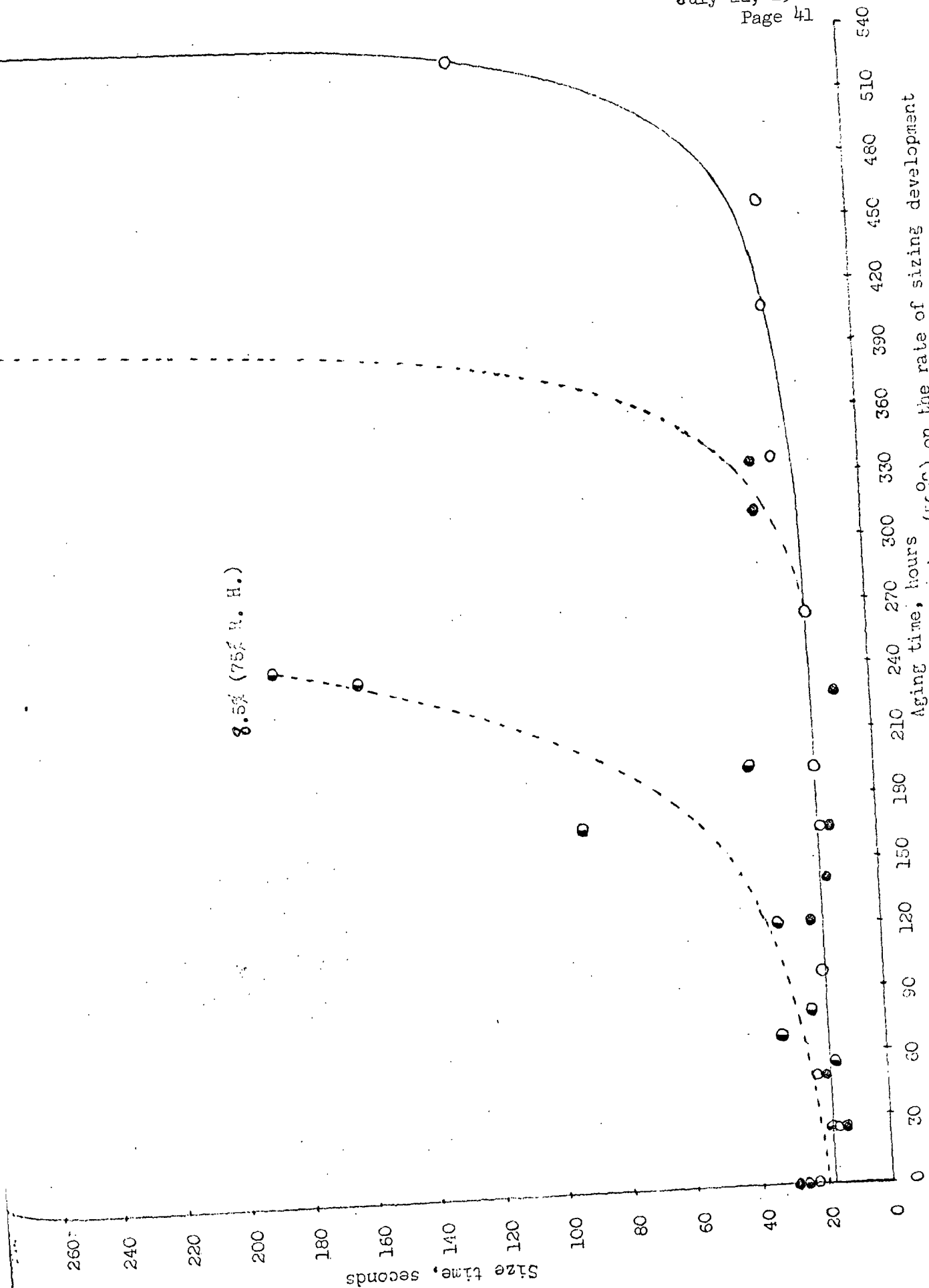


Fig. 3

Effect of moisture controlled aging (50°C) on the rate of sizing development

TABLE V

RATE OF SIZING AT MOISTURE CONTROLLED AGING AT 25°C.

Aging Time, hr.	Size Test, sec.	Av.
Moisture Content, 0.90%		
Control	23.0	
24	29.3, 15.3, 15.3, 30.6, 25.4	23.2
48	12.4, 11.6, 14.9, 29.2, 23.4	18.3
96	12.2, 16.4, 34.0, 29.3, 15.8	21.5
168	11.7, 14.9, 26.4, 19.7, 20.6	18.7
192	30.2, 12.7, 28.1, 27.5, 24.0	24.5
264	26.5, 26.1, 20.8, 13.1, 24.7	22.2
408	10.2, 12.4, 22.3, 22.2, 10.6	15.5
552	10.0, 9.6, 24.0, 28.4, -	18.0
725	21.0, 8.3, 10.9, 10.9, 12.4	12.7
1084	18.3, 16.3, 20.0, 13.7, 14.2	16.5
Moisture Content, 5.0%		
Control	29.2	
25	25.6, 17.8, 15.6, 14.9, 14.3	17.6
48	17.8, 13.4, 17.3, 15.6, 33.5	19.5
120	17.8, 20.2, 16.6, 24.7, 18.5	19.6
144	20.9, 14.1, 12.9, 28.2, 14.5	18.1
168	10.6, 12.4, 12.5, 19.2, 13.3	13.6
216	15.0, 16.3, 17.4, 12.7, 11.7	14.6
312	12.2, 11.8, 17.4, 14.2, 11.8	13.5
336	11.7, 14.7, 25.9, 16.0, 16.9	17.0
384	11.2, 13.5, 16.6, 30.4, 15.1	17.4
480	29.2, 16.0, 30.0, 32.5, 19.7	25.5
648	15.5, 19.5, 16.6, 13.5, 14.5	15.9
816	14.2, 12.6, 18.9, 14.3, 12.3	14.5
910	18.9, 26.1, 17.2, 11.6, 12.0	17.2
1128	13.2, 13.2, 12.4, 11.3, 13.3	12.7
1326	10.6, 26.7, 18.0, 23.7, 19.5	19.7
1540	17.3, 18.7, 25.8, 24.7, 31.6	23.6
Moisture Content, 9.5%		
Control	31.1	
334	27.4, 26.0, 38.3, 33.4, 25.1	30.0
501	26.7, 23.6, 57.4, 62.0, 80.8	50.1
552	16.2, 17.3, 22.1, 36.5, 17.2	21.9
573	16.2, 17.3, 22.1, 36.5, 17.2	21.9
669	14.8, 23.9, 14.8, 13.8, 21.9	17.8
833	22.5, 27.8, 44.2, 26.2, 23.5	28.8
1001	32.8, 32.8, 46.4, 46.6, 59.7	43.7
1077	20.1, 18.3, 18.1, 21.0, 51.5	25.8
1247	19.9, 20.6, 25.2, 17.5, 22.2	21.1
1485	79.1, 104, 46.0, 300+, 200	146.0
1510	35.8, 109, 40.4, 44.1, 25.9	51.0
1894	71.2, 110, 57.1, 70.2,	77.1

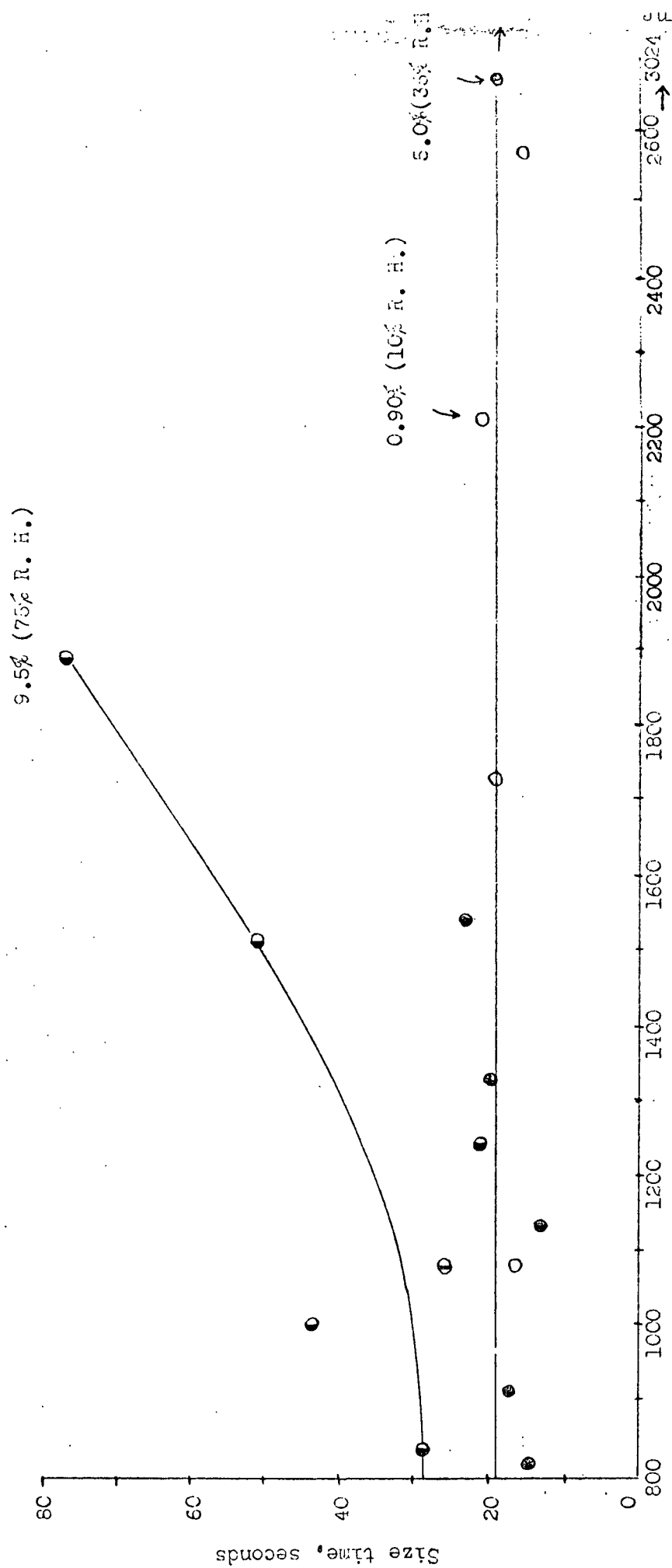


Fig. 4 Effect of moisture controlled aging (25°C) on the rate of sizing development

TABLE VI

RATE OF SIZING AT TEMPERATURE CONTROLLED AGING
 AT 10% RELATIVE HUMIDITY

Aging Time, hr.	Size Test, sec.	Av.
Temperature, 75°C. (Moisture adsorbed, 0.99%)		
Control	23.0	
24	20.1, 16.9, 22.0, 17.3, 10.9	17.4
30	62.0, 300+, 41.4, 300+, 41.4	149
31.5	114, 300+, 300+, 300+, 34.9	300+
Temperature, 50°C. (Moisture adsorbed, 0.80%)		
Control	23.0	
48	32.1, 22.0, 21.5, 12.2, 18.1	21.2
96	19.2, 21.7, 23.5, 10.9, 12.8	17.6
168	24.4, 20.5, 11.2, 11.3, -	16.9
192	21.2, 21.3, 17.6, 22.5, 8.4	18.2
264	26.5, 26.1, 20.8, 13.1, 24.7	22.2
336	13.3, 30.8, 32.7, 33.4, 21.5	26.3
408	22.4, 27.6, 28.4, 31.9, 29.0	27.9
456	28.4, 23.6, 26.6, 34.5, 24.2	27.5
528	47.7, 300+, 135, 38.4, 88.5	122
552	130, 300+, 300+, 300+, 67.1	300+
Temperature, 25°C. (Moisture adsorbed, 0.50%)		
Control	23.0	
24	29.3, 15.5, 15.3, 30.6, 25.4	23.2
48	12.4, 11.6, 14.9, 29.2, 23.4	18.3
96	12.2, 16.4, 34.0, 29.3, 15.8	21.5
168	11.7, 14.9, 26.4, 19.7, 20.6	18.7
192	30.2, 12.7, 28.1, 27.5, 24.0	24.5
264	16.9, 13.6, 20.2, 12.9, 31.0	18.9
408	10.2, 12.4, 22.3, 22.2, 10.6	15.5
552	10.0, 9.6, 24.0, 28.4, -	18.0
725	21.0, 8.3, 10.9, 10.9, 12.4	12.7
1084	18.3, 16.3, 20.0, 13.7, 14.2	16.5
1732	19.7, 12.1, 19.4, 25.3	19.1
2212	18.4, 20.2, 24.2, 21.0, 20.2	20.8

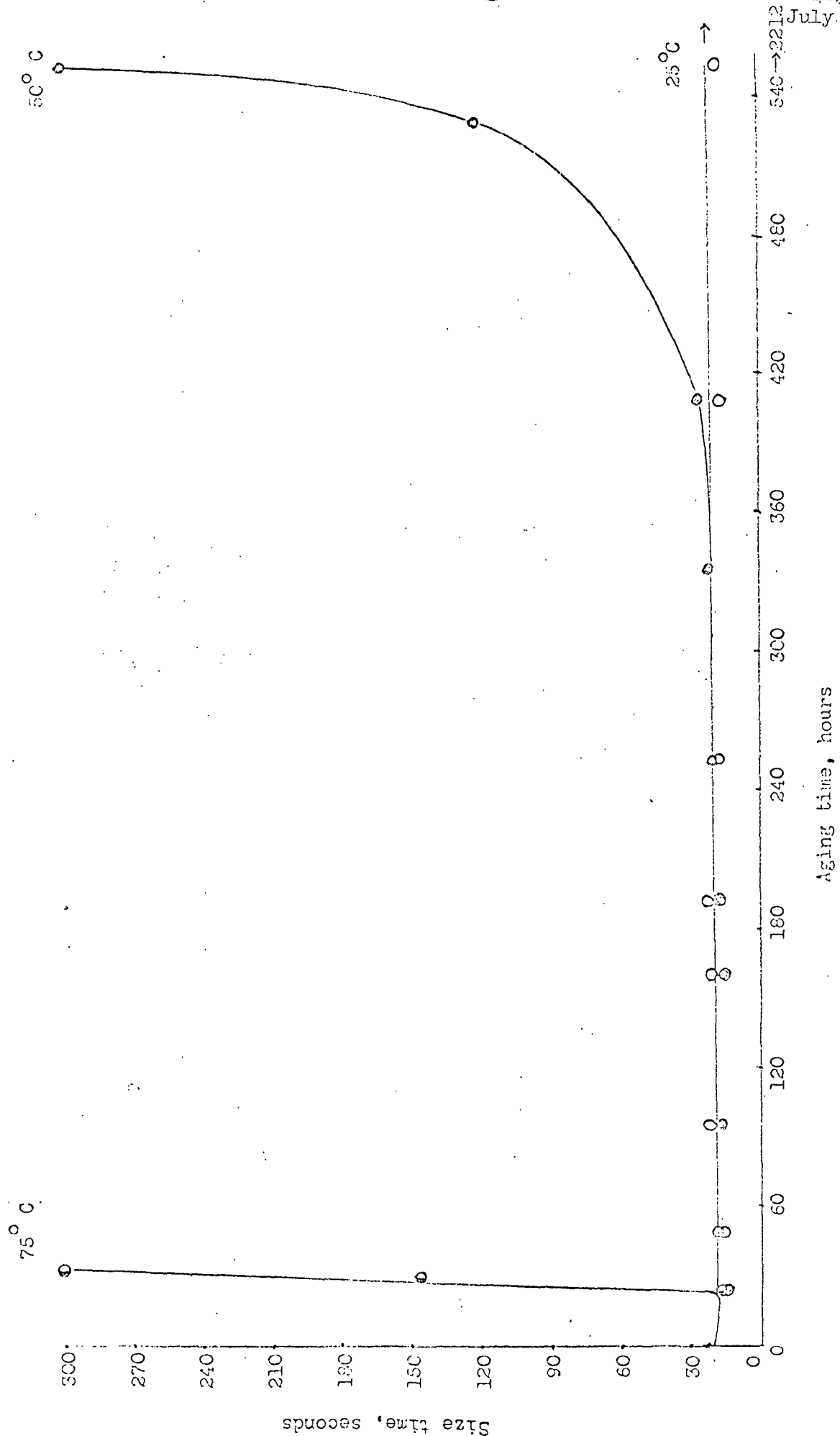


Fig. 5 Effect of temperature controlled aging at 10% relative humidity on the rate of sizing development

TABLE VII

RATE OF SIZING AT TEMPERATURE CONTROLLED AGING
 AT 35% RELATIVE HUMIDITY

Aging Time, hr.	Size Test, sec.	Av.
Temperature, 75°C. (Moisture adsorbed, 3.1%)		
Control	29.2	
15	13.2, 24.3, 25.1, 17.6, 14.4	18.9
20	33.8, 22.6, 14.0, 20.9, 30.5	24.4
24	40.8, 28.4, 25.0, 15.8, 41.1	30.2
25	92.2, 300+, 92.2, 300+, 61.5	169
Temperature, 50°C. (Moisture adsorbed, 3.9%)		
Control	29.2	
25	12.1, 14.3, 15.4, 13.1, 14.5	13.9
48	25.9, 25.8, 17.7, 15.2, 15.7	20.1
120	12.5, 26.9, 30.2, 22.8, 13.3	21.1
144	12.6, 17.1, 16.3, 13.9, 19.8	15.9
168	11.2, 13.2, 13.7, 12.6, 25.8	15.3
216	20.4, 14.2, 10.0, 13.8, 21.4	16.0
312	13.3, 36.1, 27.9, 30.8, 42.6	30.1
336	25.8, 23.3, 30.8, 21.5, 58.0	31.9
384	300+, (24.1) 300+, 300+, (38.4)	300+
Temperature, 25°C. (Moisture adsorbed, 4.9%)		
Control	29.2	
25	25.6, 17.8, 15.6, 14.9, 14.3	17.6
48	17.8, 13.4, 17.3, 15.6, 33.5	19.5
120	17.8, 20.2, 16.6, 24.7, 18.5	19.6
144	20.9, 14.1, 12.9, 28.2, 14.5	18.1
168	10.6, 12.4, 12.5, 19.2, 13.3	13.6
216	15.0, 16.3, 17.4, 12.7, 11.7	14.6
312	12.2, 11.8, 17.4, 14.2, 11.8	13.5
336	11.7, 14.7, 25.9, 16.0, 16.9	17.0
384	11.2, 13.5, 16.6, 30.4, 15.1	17.4
480	29.2, 16.0, 30.0, 32.5, 19.7	25.5
648	15.5, 19.5, 16.6, 13.5, 14.5	15.9
816	14.2, 12.6, 18.9, 14.3, 12.3	14.5
910	18.9, 26.1, 17.2, 11.6, 12.0	17.2
1128	13.2, 13.2, 12.4, 11.3, 13.3	12.7
1326	10.6, 26.7, 18.0, 23.7, 19.5	19.7
1540	17.3, 18.7, 25.8, 24.7, 31.6	23.6
2688	12.1, 19.3, 23.4, 21.4, 20.6	19.4
3024	20.8, 14.0, 16.9, 18.5, 25.1	19.1

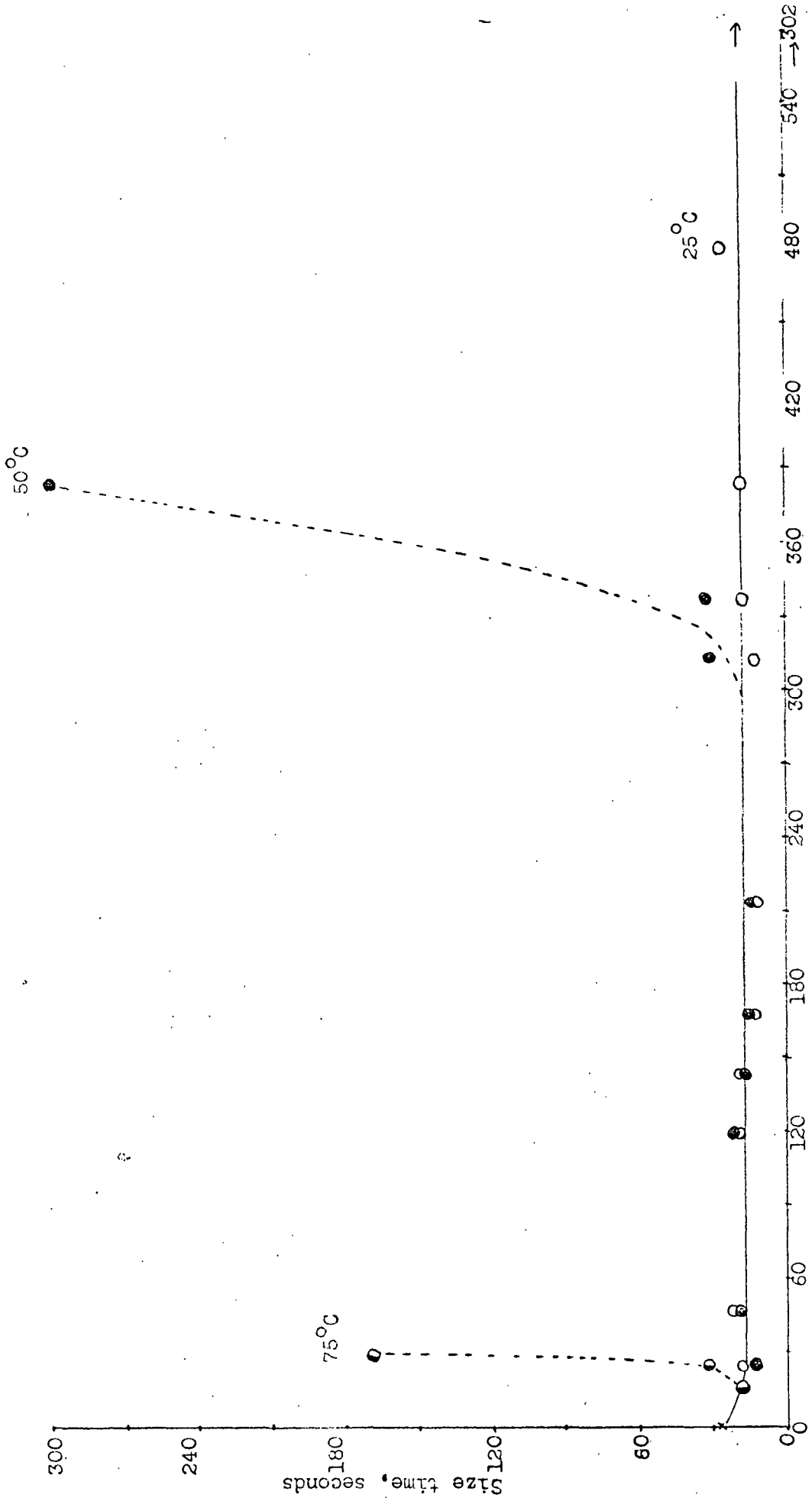


Fig. 6 Effect of temperature controlled aging at 35% R. H. on the rate of sizing development

RATE OF SIZING AT TEMPERATURE CONTROLLED AGING
 AT 75% RELATIVE HUMIDITY

Aging
 Time,
 hr.

Size Test, sec.

Av.

Temperature, 75°C.
 (Moisture adsorbed, 8.4%)

Control	26.0	
24	20.7, 16.7, 23.2, 25.3, 17.7	20.7
48	91.8, 140, 109, 251	148
54	88.0, 224, 252, 66, 184	163
71	300, 300, 300, 300, 300	300

Temperature, 50°C.
 (Moisture adsorbed, 8.4%)

Control	26.0	
24	12.8, 12.6, 22.0, 22.8, 19.5	17.9
48	14.6, 35.4, 12.5, 17.2, -	19.9
54	11.3, 16.8, 20.9, 12.6, 15.7	15.5
71	47.2, 22.9, 16.6, 30.2, 43.0	32.0
78	30.3, 12.1, 12.1, 26.9, 25.5	21.4
120	18.7, 17.8, 46.5, 51.3, 18.9	30.6
168	29.5, 249, 34.1, 50.3	90.7
192	26.9, 43.3, 23.4, 40.9, 55.6	38.0
240	123, 110, 140, 125, 300+	160
246	54.8, 300+, 186, 81.5, 300+	184

Temperature, 25°C.
 (Moisture adsorbed, 9.5%)

Control	26.0	
234	27.4, 26.0, 38.3, 33.4, 25.1	30.0
501	26.7, 23.6, 57.4, 62.0, 80.8	50.1
573	16.2, 17.3, 22.1, 36.5, 17.2	21.9
669	14.8, 23.9, 14.8, 13.8, 21.9	17.9
833	22.5, 27.8, 44.2, 26.2, 23.5	28.8
1007	32.8, 32.8, 46.4, 46.6, 59.7	43.7
1077	20.1, 18.3, 18.1, 21.0, 51.5	26.0
1247	19.9, 20.6, 25.2, 17.5, 22.2	21.1
1485	79.1, 104, 46.0, 300+, 200	146
1510	35.8, 109, 40.4, 44.1, 25.9	51.0
1894	71.2, 110, 57.1, 70.2	77.1

POSSIBLE METHOD OF INCREASING ABSORBENCY OF WOOD PULP PRODUCTS

FACTORS WHICH AFFECT THE RATE OF SIZING DEVELOPMENT

Part III. Effect of Chain Length of Fatty Acids and a Few of Their Methyl Esters and Triglycerides on Sizing

SUMMARY

Part III of the continuing study on the loss of absorbency in papers made from wood pulp was undertaken to explore the efficiency of fatty acids as sizing agents. Handsheets were prepared from bleached sulphite pulp previously extracted with a 2:1 alcohol-benzene mixture. Fatty acids ranging in concentration from 0.1 to 1.0 g. per 100 ml. were incorporated into the handsheet. Specimens containing 0.1, 0.5 and 1.0% of fatty acid based on the sheet weight were aged for several periods of time and the degree of sizing was measured by a flotation test.

Results showed that, in general, the longer chain acids developed sizing more efficiently. Triglyceride esters were effective sizing agents, but the methyl esters were not.

At the 0.1% concentration, behenic acid developed "permanent" (180 sec. +) sizing at 105°C. after 16 hours of aging. On increasing the acid concentration to 0.5%, other saturated acids, namely, myristic, palmitic, and stearic also produced permanent sizing. One percent of lauric acid was required for permanent sizing under the same aging conditions.

To further study the permanent sizing of paper with fatty acids, development of sizing by stearic acid was examined in detail. Sheets were impregnated with 1% radioactive stearic acid, and aged at

105°C., and subsequently extracted with benzene or alcohol. Extensively extracted stearic acid-treated samples retained small amounts of acid which could not be removed with either hot alcohol or benzene. The size values on these sheets were in excess of 600 seconds.

However, both the radioactivity and sizing suddenly decreased when the fully sized paper was treated with NaOH and HAc. It is believed that the NaOH treatment saponified the stearate ester groups on the cellulose.

These experiments indicated that extremely small amounts (0.012 - 0.015% based on fiber weight) of properly distributed sizing compounds were sufficient to develop well-sized paper.

EXPERIMENTAL

MATERIALS

The acids used in this work were the following:

1. n-Capric acid (Eastman Kodak Company)
2. Lauric acid (Eastman Kodak Company)
3. Myristic acid (Eastman Kodak Company)
4. Palmitic acid (Hormel Foundation)
5. Stearic acid (specially purified sample from Dr. Buchanan)
6. Arachidic acid (Eastman Kodak Company)
7. Behenic acid (Hydrofol Products)
8. Oleic acid (Fisher Scientific)
9. Linoleic acid (Hormel Foundation)
10. Methyl Myristate (Hormel Foundation)
11. Methyl Palmitate (Hormel Foundation)

12. Methyl Arachidate (Hormel Foundation)
13. Trimyristin (Matheson, Coleman and Bell Division)
14. Tripalmitin (Eastman Kodak Company)
15. Tristearin (Eastman Kodak Company)

PROCEDURES

Preparation of benzene extracted pulp and handsheets. The same procedure as described in Part II, Report No. 8 was followed.

Preparation of fatty acid benzene solution. Benzene solutions of the following concentrations, 0.1, 0.5, and 1.0% were prepared for each acid.

Sizing of benzene extracted sheet with fatty acid. The desired amount of fatty acid-benzene solution based on the weight of the pulp was applied on both sides to a 1-7/8 x 1-7/8-inch benzene extracted sheet. The fatty acid film was redistributed by spraying benzene on both sides. These samples were then ready for the aging process.

Aging of the sized samples. A test sample (a group of four sheets) was stacked in a covered ground glass weighing bottle and aged in an oven at 105°C. for the desired period. At the end of aging period the sample was immediately taken out of the weighing bottle and cooled at room temperature for about half an hour before making the sizing test.

Determination of sizing. The acid or ester sized sample, aged or unaged, was floated on water at room temperature. The uniformity of stearic acid on the sheet was observed and the time in seconds, for the water to penetrate the whole surface was recorded.

Extraction of sized samples. The sized samples were placed in a Soxhlet apparatus and extracted with 150 ml. of reagent-grade benzene or ethanol.

Determination of radioactivity by proportional counter. A

Model D-47 gas flow detector from Nuclear-Chicago Corporation was used. A base plate was specially constructed to allow two layers thick of cellophane with an opening of the same size as the micromil window. The test sample was sandwiched between these two cellophane films in order to prevent contamination of the counter. A micromil window was also used.

Determination of total C^{14} radioactivity by the Van Slyke apparatus. A circle was cut from center of the paper with a cork borer. The circle was totally oxidized by wet combustion and the carbon dioxide was collected and measured for C^{14} activity in a Bernstein-Ballentine gas-counting tube.

RESULTS AND DISCUSSION

To test the efficiency of some fatty acids, esters, and triglyceride esters as sizing agents, three different concentrations were used (0.1, 0.5, and 1% based on the weight of fibers) at four aging periods (1 hour at 50°C. and 1, 5, and 16 hours at 105°C.). Size values for the fatty acid-treated sheets are given in Table I.

Results at 0.1% acid concentration

The data in Table I show that at the 0.1% level, sizing developed significantly with stearic, arachidic, and behenic acids after 16 hours aging at 105°C. In general, the sizing effect of saturated acids increased with increase in chain length.

The unsaturated oleic acid and linoleic acid gave lower size values when compared to the saturated acid with the same number of carbon atoms. The linoleic acid developed some sizing after 16 hours aging. It has been stated that this polyunsaturated acid produces a dimerized acid containing 36 carbon atoms (1).

The three methyl esters at 0.1% level were not effective sizing agents. The sizing effect was less in the aged samples than the unaged samples, but as the carbon atoms increased, the size value slightly increased. The triglyceride esters, however, proved to be very effective sizing agents. At this level they developed a 180+ sec. - size value after 1 hour of aging at 105°C.

The extracted pulp used for Run 1 was a different batch from Run 2; hence, the sizing results were slightly different, although the same conditions were used.

Results at 0.5% acid concentration

At the 0.5% level, the size test values indicated that the longer the chain length of the acid, the better was the sizing. It is interesting to note that at this concentration, palmitic, stearic, arachidic, and behenic samples became permanently sized (over 180 sec.) after five hours aging at 105°C., while myristic acid gave the same size value after 16 hours aging. The higher the concentration of the first four sizing agents, the shorter the aging time required to reach the 180 sec. size value.

Oleic and linoleic acids at 0.5% concentration developed slightly higher size values than the 0.1% concentration after 16 hours aging, unlike the three methyl esters which showed no significant effect at any of the aging periods tested.

Of the three triglyceride esters, only tristearin gave 180 sec. size value at room temperature, after aging 1 hour at 105°C., tripalmitin also gave the same value, while the shortest chain length glyceride ester, trimyristin, did not.

Results at 1.0% acid concentration

The effect of using 1% concentration of the sizing agents indicated similar sizing trends. Behenic acid became sized at room temperature. After 16 hours aging, all saturated acids, except capric acid, became permanently sized. The three methyl esters again did not show any sizing effect, whereas the triglyceride, trimyristin, became very effective at this concentration.

It was observed that during the early part of aging, most of the acid-impregnated handsheets at the three concentration levels used exhibited a "dip" or abrupt lowering of size values; as the aging progressed the size values increased rapidly for some acids and slowly for others, as shown graphically in Fig. 1, for a few of the acids. This may be due to loss of sizing agent by evaporation at the early part of aging and as the aging proceeds, the sheet substantially picks up the sizing agent. At the same time ester formation may also take place and contribute to the higher size values.

Size values for fatty acid-treated, solvent extracted sheets are given in Table II. The results indicate that permanent sizing developed between behenic acid and cellulose after 16 hours aging at 105°C. using 0.1% acid concentration. On increasing the acid concentration to 0.5% level, other saturated acids, myristic, palmitic, and stearic, including behenic acid, became sized permanently under the same conditions of aging. Five hours aging at this concentration for any of the acids were not sufficient to size the sheet. With 1% sizing material, lauric acid became sized using the same conditions of aging, but the three methyl esters showed no indications of sizing.

To further study the permanent sizing of sheets with fatty acids, development of sizing by stearic acid was examined in detail. Sheets were treated with 1% radioactive stearic acid, aged at 105°C., and the aged samples extracted with benzene or alcohol noting the number of siphons. The results of these experiments are presented in Table III. Similar radioactivity counts were observed for all aged samples (16, 5 and 1 hr.) at 105°C. but after extraction in benzene or alcohol, only 16 hour-aged samples gave 600+ sec. size time, whereas the other two (5 and 1 hr. aged samples) gave comparatively very low size values. This indicates therefore, that during aging for 16 hours at 105°C., a chemical reaction between cellulose and stearic acid had taken place.

The same experiment showed that, inspite of extensive benzene or alcohol extractions, the radioactivity of the C¹⁴-acid treated, 16 hour aged samples became constant and the sizing permanent. Exhaustive extraction failed to reduce the size values and it is conclusively shown that the stearic acid had, therefore, chemically combined with cellulose.

The proportional counter measures only the radioactivity on the surface and to determine the total radioactivity of the sheet, the Van Slyke apparatus was used. Table IV shows some data on various materials.

It can be noted, that the top and bottom sheets had lower activities than the inner sheets. Presumably, the respective positions of the sheet in the aging container would account for the lower readings. The same effect can be found in Samples 5, 6, and 7. The inner sheet, Sample 7, showed slightly higher acid content than the upper and bottom sheets.

After exhaustive extraction and acidulated alcohol hydrolysis of Samples 8 and 9, residual stearic acid levels of 1.2 and 1.5%, (based on the amount added) respectively, were noted.

However, both the radioactivity and sizing suddenly decreased when the fully sized paper was saponified with NaOH as shown in Table V. It is believed that the NaOH treatment saponified the stearate ester groups on the cellulose.

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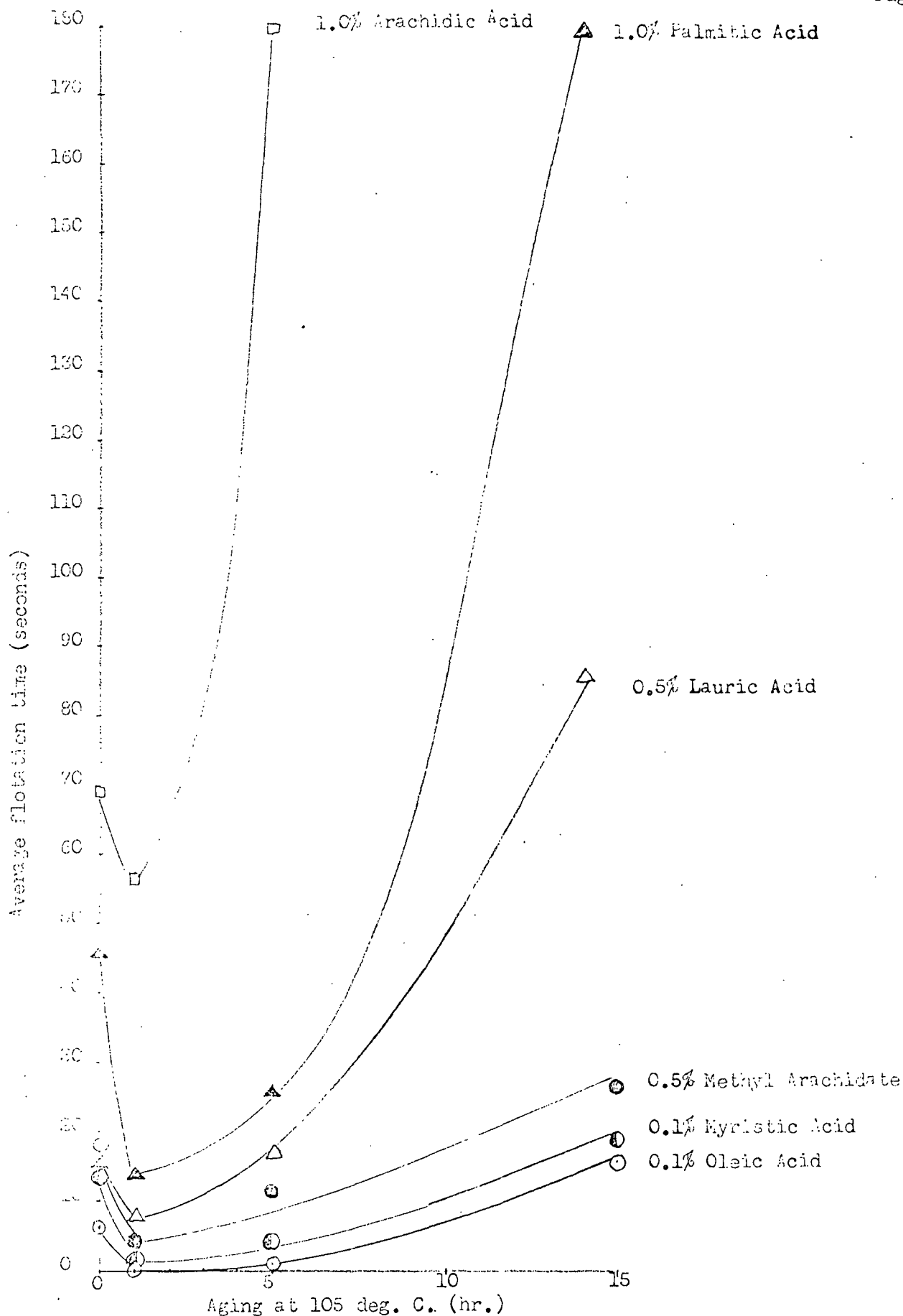


Fig. 1 Effect of various concentrations of some fatty acids and esters on sizing

TABLE I

EFFECT OF CONCENTRATION OF VARIOUS FATTY ACIDS ON SIZING

Sizing Agent	Average Flotation Time, Sec.						
	Room Temperature		Aged 1 Hr.	Aged 1 Hr. at 105°C.		Aged 5 Hrs.	Aged 16 Hr.
	Run 1	Run 2	at 50°C.	Run 1	Run 2	at 105°C.	at 105°C.
Capric acid	Inst.	8.20	0.500	3.00	8.60	9.80	9.60
Lauric acid	3.00	4.60	Inst.	2.60	14.3	Inst.	13.4
Myristic acid	13.2	28.1	5.40	1.90	7.70	4.40	18.6
Palmitic acid	16.7	21.1	20.0	11.1	9.20	13.1	16.4
Stearic acid	14.6	29.4	18.0	17.2	6.00	25.7	98.3
Arachidic acid		40.9	37.6	79.3		189	180+
Behenic acid	23.8	128	25.2	25.9	51.5	39.5	180+
Oleic acid	6.10	4.10	4.80	0.400	0.400	1.10	15.9
Linoleic acid	1.60	6.30	0.900	2.10	5.60	Inst.	43.9
Methyl myristate	4.00	8.20			2.20	Inst.	0.500
Methyl palmitate	4.60	8.80		0.400	Inst.	Inst.	3.30
Methyl arachidate	9.30	22.4		4.70	2.10	Inst.	8.80
Trimyristin	22.4		5.40	7.10			
Tripalmitin	12.4			180+			
Tristearin	12.1		6.60	180+			
Capric acid	2.30	15.0	3.30	1.60	7.30	8.50	Inst.
Lauric acid	14.7	16.5	3.50	2.30	7.90	16.7	86.1
Myristic acid	54.5	88.5	20.1	1.50	2.90	19.0	180+
Palmitic acid	56.9	71.3	33.2	7.90	13.7	180+	180+
Stearic acid	33.6	105	36.6	16.7	65.1	180+	180+
Arachidic acid		60.6	78.7	78.4		180+	180+
Behenic acid	132	180+	180+	180+	180+	180+	180+
Oleic acid	7.50	13.3	6.30		16.8	31.4	45.9
Linoleic acid	Inst.	6.10	4.30	5.60	14.4	19.4	52.2
Methyl myristate	2.70	0.400		3.30	Inst.	Inst.	6.40
Methyl palmitate	4.80	3.10		2.30	9.60	0.600	13.0
Methyl arachidate	18.4	28.6		4.70	Inst.	11.5	26.8
Trimyristin	23.0			9.20			
Tripalmitin	102			180+			
Tristearin	180+			180+			
Capric acid	3.20	16.6	Inst.	Inst.	6.30	Inst.	66.3
Lauric acid	21.3	19.5	Inst.	Inst.	6.30	Inst.	180+
Myristic acid	48.9	43.6	2.20	Inst.	11.9	Inst.	180+
Palmitic acid	95.3	46.4	40.8	6.50	13.6	26.1	180+
Stearic acid	68.6	68.0	53.6	16.1	57.2	180+	180+
Arachidic acid	69.5	63.3	54.6	56.0		180+	180+
Behenic acid	180+		180+	180+		180+	180+
Oleic acid	6.60	9.20	Inst.	Inst.	Inst.	Inst.	1.5
Linoleic acid	2.40	10.6	Inst.	9.60	Inst.	Inst.	73.1
Methyl myristate	2.10	5.30		Inst.	Inst.	Inst.	Inst.
Methyl palmitate	6.90	9.50		0.400	1.90	Inst.	Inst.
Methyl arachidate	23.8	26.9		14.7	4.90	Inst.	Inst.
Tristearin	103			263			

TABLE II

Comparison of Sizing Before & After Benzene Extraction
 of Fatty Acid Treated and Aged Samples

Fatty Acid	Ave. Flotation Sizing Time in sec.					
	Aged 1 hr. at 105° C.		Aged 5 hrs. at 105° C.		Aged 16 hrs. at 105° C.	
	Before Ex.	After Ex.	Before Ex.	After Ex.	Before Ex.	After Ex.
0.1% Capric					32.2	20.7
Lauric					36.0	15.0
Myristic					41.0	18.6
Palmitic					39.0	15.9
Stearic			51.4	16.3	121	103
Behenic			65.2	19.4	180	180+
Oleic			26.8	15.8	38.5	24.1
Linoleic			24.9	32.4	66.5	61.8
Control					19.6	
0.5% Capric			34.2	23.8	22.2	15.4
Lauric			42.4	30.1	109	90.0
Myristic			44.7	30.4	180+	180+
Palmitic			180+	26.1	180+	180+
Stearic			180+	23.2	180+	180+
Behenic			180+	31.3	180+	180+
Oleic			57.1	75.5	68.5	77.8
Linoleic			45.1	70.7	74.8	90.9
Control			21.5		22.6	
1.0% Capric	27.8	23.3	15.8	15.2	88.9	111
Lauric	30.8	20.0	14.1	11.2	180+	180+
Myristic	33.4	18.5	16.5	14.6	180+	180+
Palmitic	35.1	13.7	51.8	16.6	180+	180+
Stearic	78.7	17.4	180+	12.1	180+	180+
Oleic	17.4	11.0	12.4	11.6	24.1	68.9
Linoleic	19.7	26.8	15.9	37.9	35.1	143
Me. Myristate	17.2		9.4	8.20	7.40	8.00
Me. Palmitate	23.4		13.2	7.40	12.1	6.80
Me. Arachidate	27.4		15.5	7.50	11.5	7.20
Control	21.5	15.8	25.7	14.3	22.6	12.5

TABLE III

Effect of Aging and Exhaustive Solvent Extraction of
C₁₄ Stearic Acid Sheets on Radioactivity and Sizing

	Fresh Sample After Aging at 100°C.			Radioactivity After Extraction, c/m					Flotation Test, (sec.) of Extracted Sample					
	c/m	Hours	c/m	(3)	(6)	(9)	(12)	(33)	(0)	(3)	(6)	(9)	(12)	(33)
A. Benzene extraction	11233	16 5 1	4708 7784 8657	495 812 712	410 482 431	355 363 322	255 208 190	175 163 161	600+	600+	600+	600+	600+	600+
B. Benzene extraction	10818 10818 11052 10449	16 5 1	5043 5794 7288	(3) 501 300	(9) 352 284	(147) 175	(207) 122	(297) 125	(3) 29.8 20.8	(9) 20.0 13.4	(147) 600+	(207) 600+	(297) 600+	(3) 600+
C. 95% Ethanol extraction	10818 8545 10975	16 5 1	5097 5167 7348	(3) 104 92	(9) 96 46 21	(37) 66	(147) 57	(177) 63	(3) 600+	(9) 600+	(37) 600+	(147) 600+	(177) 600+	(3) 10.5 14.8 6.40 7.60

- Note: 1. Each figure given is the average of 4 determinations, except the fresh sample in A, which is the average of 12.
2. The figures enclosed in parentheses indicate the number of siphons during the extraction.
3. Radioactivity is expressed in counts per minute (c/m).

TABLE IV

MEASUREMENT OF RADIOACTIVITY ON VARIOUS
 AGED SAMPLES BY VAN SLYKE APPARATUS

Sample No.	Sheet Position in Aging Container	Condition of 1% C^{14} Stearic Acid Treated Sheet	Specific Activity c.p.m./ μ g.C.	Stearic Acid Left After Aging, % (based on amount added) (based on fiber weight)	
1	1 (top)	Aged 16 hr. at 105°C.	2313	45.8	0.458
2	2	Aged 16 hr. at 105°C.	3592	71.1	0.711
3	3	Aged 16 hr. at 105°C.	3664	72.5	0.725
4	4 (bottom)	Aged 16 hr. at 105°C.	2512	49.7	0.497
5	1	Aged 16 hr. at 105°C., and extracted in C_6H_6 for 14 siphons	95.3	1.89	0.019
6	4	Aged 16 hr. at 105°C., and extracted in C_6H_6 for 14 siphons	91.6	1.81	0.018
7	2	Aged 16 hr. at 105°C., and extracted in C_6H_6 for 14 siphons	114	2.26	0.023
8	1	Extracted and hydrolyzed	77.2	1.53	0.015
9	1	Extracted and hydrolyzed	60.4	1.20	0.012
10		Without aging	5053	100	
11		Stock Solution	1.982×10^6		

Note: The first four samples were stacked up and aged in a ground glass-weighing bottle, with sample No. 1 placed on the top and the fourth one at the very bottom. Sample 8 was extracted in benzene for 297 siphons and then hydrolyzed in a solvent of 4 cc. concentrated HCl in 1 liter 95% ethanol for several hours. Sample 9 was extracted in 95% ethanol for 177 siphons before hydrolysis in the same solvent mentioned above for several hours. These two samples are the 16 hr.-aged samples listed in Table IV.

TABLE V

The Effect of Saponification on Cellulose Stearate Product

	<u>Sample 1</u>	<u>Sample 2</u>
Activity before saponification	125	70
Activity after saponification*	42	40
Flotation size (sec.) before saponification	600+	600+
Flotation size (sec.) after saponification	8.40	8.70

Note: Sample 1 was 1% C^{14} stearic acid treated and extracted in C_6H_6 for 297 siphons before being saponified.

Sample 2 was 1% C^{14} stearic acid treated and extracted in C_2H_5OH for 177 siphons before being saponified.

The activity of these samples was determined by a proportional counter.

*These samples were soaked in 0.1N NaOH for overnight, and then washed with deionized water, neutralized with 0.1N HAC and washed acid free with water.