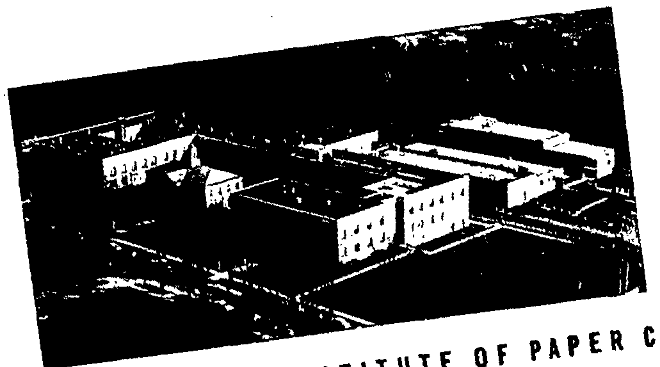

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

Report Eleven

Project 2256

Monthly Progress Report

to

U. S. ARMY CHEMICAL CENTER PROCUREMENT AGENCY

Report Period: July 29, 1961 to August 28, 1961

September 25, 1961

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

DEVELOPMENT OF AN IMPROVED DIFFUSION BOARD MATERIAL

Project 2256

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THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

DEVELOPMENT OF AN IMPROVED DIFFUSION BOARD MATERIAL

SUMMARY

Extrapolation of isothermal water absorption curves for charcoal-loaded board to 100% relative humidity indicates that the minimum water absorption that can be approached through sizing would be approximately 9.5% by volume. Comparison of the isotherms for charcoal-loaded board and blank samples suggests some interaction between the charcoal and the fibers, particularly at high humidities.

Measurements of the pH of the cold water extract from aged boards did not indicate the existence of any gross acid conditions which might account for the deterioration of the board; this does not preclude the possibility of some localized process involving the presence of acidic material.

Accelerated aging for one week under tropical conditions resulted in deterioration of the cyanogen chloride gas lives of all sized boards and all unsized boards with the smallest change in the unsized board formed from repulped newspaper.

Boards containing additions of the fungicides tributyltin oxide and copper pentachlorophenate were submitted to the Army Chemical Center for gas life testing. Tributyltin oxide was used in the form of three dispersions, C-Sn-6, C-Sn-9, and C-Sn-10 obtained from the Metal and Thermit Corporation. Copper pentachlorophenate was used according to the sequestering method covered by Monsanto's U. S. Patent No. 2,904,466. Surface treatment has been considered as a means of fungicide application; boards sprayed with dispersions of copper pentachlorophenate and copper-8-quinolinolate were submitted for gas life tests.

Preliminary inquiries have been addressed to commercial producers of insulation board in order to initiate negotiations for the commercial run.

ISOTHERMAL MOISTURE ABSORPTION

The method commonly used in the insulation board industry and adopted for evaluation of water repellency in this program involves determination of gain in weight of a board when immersed in water under standard conditions. This test includes resistance to liquid water penetration (which sizing should control) and exposure to high humidity (which conventional sizing cannot control). In order to determine how much absorption of water might be expected from high humidity exposure, a determination of moisture isotherms was initiated.

The minimum moisture take-up expected for a sized board in contact with liquid water would be equal to the amount of moisture absorbed by the board in the form of vapor at the 100% relative humidity concentration at an air temperature equivalent to the temperature of the liquid water. By determining the isothermal water absorption at various humidities, curves can be drawn and extrapolated approximately to 100% relative humidity--since it is not practical to control a water vapor-saturated atmosphere. Previous liquid water absorption tests were run at 73°F.; consequently, these tests were also run at 73°F. In these tests the water adsorption properties of the charcoal was also adjudged by testing a blank board which contained no charcoal.

The moisture take-up at constant temperature was determined at three relative humidity levels for three samples of board formed from Wood Conversion Company pilot run stock. One sample was a blank containing no charcoal or size additions, the second sample contained 19% charcoal, and the third sample contained 18.5% charcoal and 0.5% Aquapel 360 and 0.2% Kymene 557 additions (Group

3 of Bauer Bros. pilot run). The determination was run in the following manner: Six specimens of each sample were dried at 160°F. for 24 hours, placed in weighing bottles and cooled to 73°F. Two specimens from each sample were conditioned at 50% R.H., and 73°F.; at 92% R.H., and 73°F.; and at 97% R.H., and 73°F. to constant weight. The moisture content was calculated by dividing the weight of the water absorbed by the dry weight of the sample.

The values obtained in these determinations are given in Table I and the isotherms are shown in Fig. 1 along with the per cent water absorbed by the charcoal assuming no interaction between the charcoal and the fibers. The fact that the calculated absorption for the charcoal is greater at 92% R.H. than at 97% R.H. is an indication of some interaction possibly becoming pronounced as the saturation point of the charcoal is approached. The charcoal-loaded boards have almost identical isotherms, meaning practically no reduced water absorption due to the Aquapel-Kymene sizing. Extrapolation of the curves for the charcoal-loaded board to 100% relative humidity gives an intercept of 28% water absorption or 9.5% absorption by volume for a 21 lb./cu. ft. board. This 9.5% absorption by volume can be construed as the minimum water absorption possible with use of any sizing system that does not physically seal the board; 24-hour water absorption values as low as 13% have been achieved with Aquapel-Kymene sizing (Report 9; Bauer Bros. pilot run).

TABLE I

ISOTHERMAL WATER ABSORPTION

(Boards Formed From Wood Conversion Co. Pilot Run Pulp)

Sample	Charcoal Content, % by wt.	Sizing Additions, % ovendry fiber	Water Absorbed By Board at 73°F., % by wt.			Water Absorbed By Charcoal at 73°F. (Calculated), % by wt.		
			50% R.H.	92% R.H.	97% R.H.	50% R.H.	92% R.H.	97% R.H.
Blank	--	--	6.8	19.3	23.5	--	--	--
2256-96-5	19	--	9.0	21.6	24.8	18.4	31.6	30.5
PR-3-3	18.5	0.5% Aquapel 360 0.2% Kymene 557	8.8	21.5	24.6	17.8	31.4	29.2

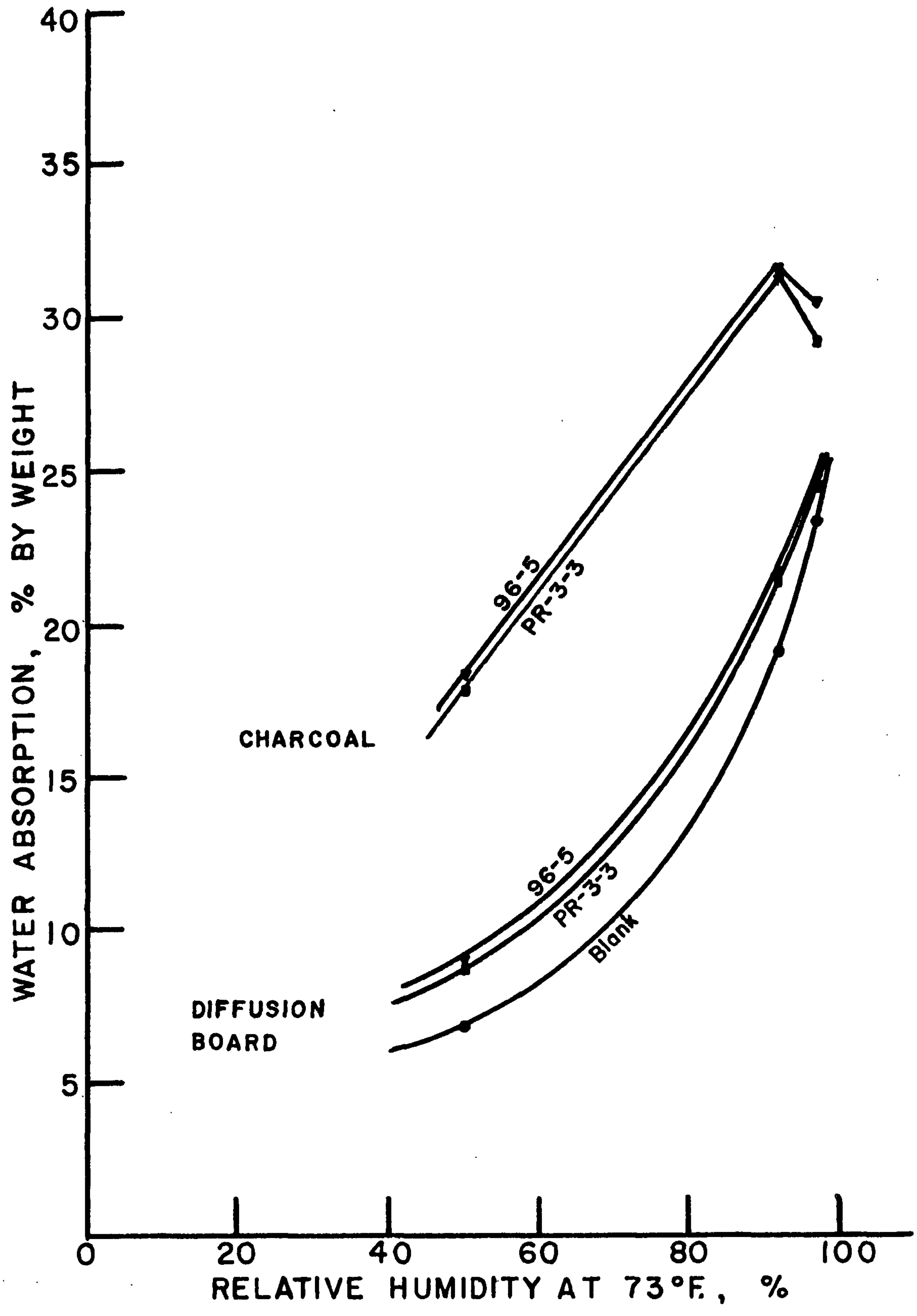

Figure 1. Water Absorption Isotherms

AGING

The effect of storage in ambient conditions was discussed in Report Ten. The next logical steps in the study of aging are the determination of any of the physical and/or chemical changes taking place during the aging process which might characterize the process or provide an index of degree of deterioration or potential for deterioration and the study of aging in a controlled environment. The final evaluation of an aged board is its protective capabilities considered quantitatively for cyanogen chloride protection in terms of the calculated critical bed loading (the zero gas life intercept at a straight line having a slope of 26.5 min./g./100 sq. cm. in a plot of charcoal loading *versus* CK gas life).

EFFECT ON pH

The pH of samples of aged boards determined according to the TAPPI T-435 procedure is given in Table II. It was thought that, should the processes of aging involve gross pH changes throughout the board, the board would become acidic. Unsized boards formed from Minnesota and Ontario pulp and repulped newspaper and sized boards formed from a mixture of Wood Conversion Company stocks were tested. There was no noticeable difference in the pH's of the boards and all of the pH's were above 7; this includes a sample of repulped newspaper board which seemed to be little affected by aging. The only available indications of the alkalinity of the unaged boards were pH measurements of the slurries from which the boards were formed; these pH's would be higher than the pH's of the board product because of the alkalinity of the water (pH 9) used in the slurries. If acid conditions are involved in deterioration of the charcoal activity during storage, they are local and masked by the pH of the other components of the board.

TABLE II

pH OF AGED BOARDS

Sample 2256	Pulp	Sizing, % based on ovendry fiber	Aging, days	Charcoal Loading, g./100 sq. cm.	Critical Bed, g./100 sq. cm. Unaged	Critical Bed, g./100 sq. cm. Aged	pH[a]	Forming pH
17-6	Minnesota & Ontario	--	190	5.2	4.0	4.9	7.2	7.3
33-4	Repulped news.	--	180	6.6	4.6	4.8	7.2	7.6
76-2	Wood Conversion Co.	0.5% Aquapel 486	110	5.7	4.3	4.8	7.3	8.5
76-9	"	0.1% Aquapel 486 0.5% Cato 8	110	6.2	5.2	5.4	7.2	8.4
78-15	"	0.1% Aquapel 360	110	5.8	4.5	5.1	7.2	8.2
78-21	"	0.5% Aquapel 360 0.2% Kymene 557	110	5.7	4.8	5.6	7.1	8.2

[a] pH of cold water extract -- TAPPI T-435

ACCELERATED AGING

A study of accelerated aging, carried out under tropical conditions was mentioned in Report Ten. Boards, sized and unsized, formed from either of two pulps, washed and unwashed, were submitted for evaluation. Results are presently available for boards aged for one week in the following manner: each specimen was conditioned to 80% R.H. and 80°F., sealed in a bag and stored for one week at 113°F. The results of initial and aged CK life tests on these samples are given in Table III; critical beds were calculated from an assumed charcoal content of 19% since actual charcoal contents were not available. Considering initial critical beds, the best values were obtained for the unsized boards made with washed Wood Conversion Co. pulp. Unsized boards made with repulped newspaper had slightly higher initial critical beds and the unsized boards from unwashed pulp were still higher. Initial critical beds for the sized boards tended to be somewhat higher than those for the unsized boards of the same pulp.

On aging, the least change was found in the unsized repulped newspaper board. Sized board from the same stock deteriorated much more drastically. Aging of the unsized board of Wood Conversion Co. pulp was more marked and not helped by washing. Addition of sizing increased loss of life on aging slightly.

The critical bed data for the sized and unsized repulped newspaper board suggests that the Aquapel-Kymene sizing system produces rapid deterioration of the charcoal activity. However, it is possible that very few chemical bonds are established between the fibers of this pulp and the Aquapel, resulting in the presence of a large amount of "free" Aquapel which is easily hydrolyzed. An effect of the Aquapel-Kymene system on aging of the boards formed from the Wood Conversion Company pulp is also apparent but not to the degree indicated with the repulped newspaper.

TABLE III

EFFECTS OF AGING FOR ONE WEEK--TROPICAL CONDITIONS

Sample 2256-	Pulp	Sizing[a]	CK Gas Life, min. Initial Specimen	CK Gas Life, min. Aged Specimen	Charcoal Loading,[b] g./100 sq. cm. Initial Specimen	Charcoal Loading,[b] g./100 sq. cm. Aged Specimen	Critical Bed, g./100 sq. cm. Initial Specimen	Critical Bed, g./100 sq. cm. Aged Specimen
NP-1-122	Repulped newspaper	yes	22.0[c]	8.0	5.5	6.8	4.7[c]	6.5
NP-2-122	" "	yes	58.0	10.0	5.2	5.4	3.0	5.0
NP-3-122	" "	no	77.0	57.0	6.1	5.5	3.2	3.4
NP-4-122	" "	no	64.0	57.0	5.2	5.8	2.9	3.7
PR-1-127	Unwashed Wood Conv. Co. pilot run pulp	yes	50.0	11.0	5.7	5.8	3.8	5.4
PR-2-127	" "	yes	52.0	9.0	5.8	5.7	3.8	5.4
PR-3-127	" "	no	62.0	29.0	5.7	6.1	3.4	5.0
PR-4-127	" "	no	58.0	18.0	6.3	5.9	4.1	5.2
PRW-1-127	Washed Wood Conv. Co. pilot run pulp	yes	60.0	7.0	5.2	5.5	2.9	5.2
PRW-2-127	" "	yes	73.0	7.0	5.7	5.3	2.9	5.0
PRW-4-127	" "	no	76.0	37.0	5.3	5.7	2.4	4.3
PRW-5-127	" "	no	66.0	28.0	5.1	5.2	2.6	4.1

[a] Sizing additions: 0.5% Aquapel 360; 0.2% Kymene 557 (based on ovendry fiber).

[b] Based on assumed charcoal content of 19.0%.

[c] Bad value, poor board formation.

FUNGICIDES

Several fungicides have been evaluated to determine their utility and compatibility in diffusion board (see Report 8). Of these materials, sodium pentachlorophenate (Dowicide G) has been ruled out since its use requires acidification of the pulp slurry. While the other materials did not produce satisfactory results, there were indications that they might be rendered satisfactory by modifying dispersing medias or methods of treatment. Samples of diffusion board were given to a representative of the Scientific Chemicals Company; their laboratory will attempt to make up a formulation of copper-8-quinolinolate that would be suitable for use in diffusion board under alkaline conditions.

Three fungicides and two methods of treatment were evaluated at the Institute during this reporting period. A series of boards containing additions of tributyltin oxide and copper pentachlorophenate was made from the Wood Conversion Company pilot run pulp. A series of boards, also formed from this pulp, was treated by spraying dilute dispersions of copper pentachlorophenate and copper-8-quinolinolate. These materials were to be evaluated in terms of gas-life only as the time element involved would not allow any mildew tests. No gas life data is available at this time.

Tributyltin oxide has shown some promise as an effective fungicide which might be compatible with the gas life properties. In the previous work in which the TBTO showed promise, acetone was used as a solvent for the pure material. Erratic results indicated that the TBTO did not disperse properly when added to a pulp slurry in an acetone solution. It was also thought that the acetone may have affected the gas life of the board; however, subsequent tests of boards containing acetone additions equal to the volume used as a solvent for TBTO additions showed no losses in cyanogen chloride gas life (see Table IV). With the thought that better dispersion would allow the use of smaller additions of the TBTO, a series of boards were made with additions of three TBTO dispersions obtained from the Metal and Thermit Corporation. These dispersions, labeled C-Sn-6, C-Sn-9, and C-Sn-10 contained 5, 20, and 80% TBTO, respectively; C-Sn-6 also contained 25% N-alkyl dimethyl benzyl ammonium chlorides. TBTO addition levels, based on ovendry fiber, of 0.2 and 0.5% were used.

TABLE IV

EFFECT OF ACETONE ON CYANOGEN CHLORIDE GAS LIFE

Sample 2256-	Acetone Addition	CK Gas Life, min.	Charcoal Loading (assumed), g./100 sq. cm.	Calculated Critical Bed, g./100 sq. cm.
94-1	Blank	43.8	5.0	3.3
101-1	80 cc. after charcoal	49.9	5.0	3.1
101-2	80 cc. before charcoal	45.2	5.0	3.3

A sequestered solution of copper pentachlorophenate was made according to the method covered by Monsanto's U. S. Patent No. 2,904,466 (September 15, 1959). In this method, equal amounts of hydrous copper sulfate and tetrasodium pyrophosphate are dissolved in water and to this is added sodium pentachlorophenate at a 2.5:1 ratio to the copper sulfate. This suspension is "broken" by the presence of cellulose fibers, resulting in the precipitation of the copper pentachlorophenate on the fibers. This solution was added to pulp slurries in amounts equivalent to 1.0 and 2.0% copper pentachlorophenate based on ovendry fiber.

A DeVilbiss spray gun, operating on 20 p.s.i. air, was used to apply fungicidal solutions to the surfaces of otherwise untreated, dried boards. The gun was calibrated by determining the amount of water sprayed in a given time over a given area a fixed distance from the spray nozzle. Sized and unsized boards were treated with solutions of copper pentachlorophenate and copper-8-quinolinolate (Cunilate no. 2419). The sized boards contained 0.5% Aquapel 360 and 0.2% Kymene 557 additions, based on ovendry fiber. The fungicide treatment levels were 0.1% copper pentachlorophenate and 0.13% copper-8-quinolinolate based on ovendry fiber weight. The board samples were dried for one hour at 105°C. immediately after treatment and then sealed in individual bags.

All of the boards comprising this series were originally dried for 3 hours at 105°C. and sealed in individual polyethylene bags. Two untreated blanks were also formed as controls.

NEGOTIATION FOR PRODUCTION RUN

One of the requirements of this contract is production of 15,000 square feet of board on commercial equipment, using an acceptable formulation. Inquiries were addressed to a number of commercial producers of insulation board to determine their possible interest in co-operating in such a run. Several indicated that various factors made their situation unfavorable for such runs. Three companies (Minnesota and Ontario Paper Co., Wood Conversion Co., and Simpson Timber Co.) indicated that they would be willing to co-operate and would write further details on the basis for such co-operation.

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