

5—Ferric ion is adsorbed to such an extent that it will carry the particles over from a negative charge through the isoelectric point to a condition of positive charge in a manner analogous to the reversal of charge on albumin particles.

6—From the experiments with ferric chloride and ferric nitrate it is apparent that both ions of an added electrolyte are effective in precipitation of the charged particles.

7—The decrease in stability of these emulsions upon the addition of ether is probably due to the solvent action of the ether on the asphalt rather than to any increase in the difference in density of the two liquid phases. An ether-carbon disulfide mixture of the same gravity as the emulsion will discharge the water.

8—The action of certain commercial treating compounds is probably due to the fact that they are hydrophile colloids. A hydrophile colloid should discharge an emulsion formed by the use of a hydrophobe colloid, while a hydrophobe colloid should discharge an emulsion formed by the use of a hydrophile colloid.

#### ACKNOWLEDGMENT

In conclusion, the author wishes to thank Mr. E. T. Gregg for aid and helpful suggestions, and Dr. F. M. Seibert and Mr. J. Van der Henst for procuring samples.

### TESTING THE MILDEW RESISTANCE OF TEXTILES<sup>1</sup>

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A study of the fundamental factors determining the effectiveness and durability of processes of waterproofing and mildewproofing textile fabrics, such as cotton duck and cotton canvas, was undertaken with the primary object of finding simple formulas and methods for treating cloth which are applicable for small-scale use on the farm and also suitable for use by commercial treating plants. Prerequisites for successful work on the main problem are, of course, suitable methods for determining water and mildew resistance. The method here described, which is not regarded as final but subject to improvement with experience and greater knowledge of the problems involved, has been used for the past two years and has proved to be useful in judging the probable serviceability of mildew-resistant treatments. The methods used for testing the water resistance of fabrics are described in a separate paper.<sup>2</sup>

Mildewing is due to the development of various mold growths on and in the fabrics. The number of species responsible for the deterioration is large, but chief among them are species of *Alternaria*, of *Cladosporium*, and some *Mucors*. The simultaneous occurrence of different kinds of molds seems to play an important part, and the production of pink and yellowish discolorations is probably due, at least in some cases, to the growth of both a *Mucor* and a mold pro-

ducing a substance having a pink appearance in alkaline or neutral reaction and a yellow one in an acid reaction.

Gueguen<sup>1</sup> is of the opinion that the spores causing the mildewing of fabrics are usually introduced into the fibers by the dead parts of the parent cotton plant, where they have been either in a dormant or germinating state, and concludes that mildew is hardly ever due to contamination of the fabric after weaving.

The presence in the air of spores of cellulose-destroying fungi has been demonstrated by McBeth and Scales,<sup>2</sup> who have isolated from plates exposed to air contamination over a dozen cellulose-destroying organisms, among which *Cladosporium herbarum* has been identified. Davis, Dreyfus and Holland<sup>3</sup> have shown that astonishingly large numbers of mold spores rain into the mill vats containing sizing materials used on the component threads, thereby becoming introduced into the woven fabric.

We have repeatedly mildewed pieces of treated and untreated fabrics by inoculating their surfaces with pure cultures of *Cladosporium*, *Alternaria*, and other molds, and have found that, under laboratory conditions, converted canvas may be completely destroyed by several species of *Aspergillus*.

Sterilized duck inoculated with spores and mycelial fragments of species of *Alternaria* and of *Cladosporium* and incubated for two weeks, developed mold growth which, at the end of another two weeks, entered deeply into the fabric. Furthermore, heavy fabrics, subjected to certain finishing processes having a sterilizing effect on the preëxisting mold spores and mycelial fragments, readily mildew under favorable field conditions. It is clear, therefore, that even canvas apparently free from original mold impregnation will mildew if exposed to air contamination and to conditions encouraging mold growth.

#### METHODS USED TO DETERMINE MILDEW RESISTANCE

Tests for mildew resistance of fabrics have been in use heretofore. One, occasionally followed, is, briefly, to bury a sample of the cloth under ground at a depth of 12 to 15 in. for a period extending over one month. The ground is kept moist by occasional watering. The condition of the fabric at the end of the test period is considered to indicate the degree of mildew resistance.

This method may give valuable information regarding the resistance of fabrics to bacterial action, but its value for determining mildew resistance is questionable. Waksman<sup>4</sup> found that soil samples taken from a depth of 12 to 30 in. on plating out developed only *Zygorhynchus*, and that *Aspergillus*, *Alternaria*, *Cladosporium*, *Penicillium*, and other organisms commonly present in the soil had not appeared in the plates in 24 hrs.; while in the upper soil strata there may be 1,000,000 fungi per gram of soil. This, really, is a small number of organisms,

<sup>1</sup> *Compt. rend.*, **159** (1914), 781.

<sup>2</sup> U. S. Dept. of Agr., Bureau of Plant Industry, *Bulletin* **266**, pp. 24-25.

<sup>3</sup> "Sizing and Mildew in Cotton Cloth," **1880**, Palmer and Howe, Manchester.

<sup>4</sup> *Science*, N. S., **44** (1916), 320-23.

<sup>1</sup> Read at the 57th Meeting of the American Chemical Society, Buffalo, N. Y., April 7 to 11, 1919.

<sup>2</sup> *This Journal*, **12** (1920), 26.

as compared with the many millions of bacteria usually present. Canvas buried under ground would, therefore, be subject to bacterial rather than to fungus attack. That this is so, is indicated by the fact that cotton duck coated with a thin layer of paraffin remained practically unattacked when buried under ground for nearly a month, whereas mildew developed in less than a month when inoculated in the laboratory.

Furthermore, since it is generally recognized that different soils have different microbial flora, that species present under one combination of conditions may be absent under others even in the same soil, it is not practicable to standardize this method of testing.

Another method is to roll together several samples of the cloth to be tested with layers of fresh horse manure and of sawdust and keep for about a month in a moist condition. At the end of the period the condition of the cloth is observed, and if no deterioration is evident, the samples are again rolled up and left for another month or two.

Haubner,<sup>1</sup> Henneberg and Stohmann,<sup>2</sup> Knieriem,<sup>3</sup> Choukevitch<sup>4</sup> and others have shown that cellulose is fermented by bacteria in the intestinal tract of practically all animals, man included. It is reasonable to think, therefore, that cellulose-destroying bacteria abound in fresh feces, but that molds are practically absent. This statement has been confirmed in this laboratory. Finally, this procedure obviously cannot be standardized, and, because of its offensive character, is not suited for laboratory work.

The simplest and most useful method heretofore used is that of suspending the test sample in a closed jar containing some water. The jar is kept in a dark, preferably warm, room for 5 to 7 days. At the end of this period, the test is discontinued. This test, though subject to some criticism, is better than those previously described, since it can be easily conducted under standard conditions. The period of incubation usually employed, however, is entirely too short. We have found that certain fabrics, which have remained unattacked by molds for over a week, have proved to be susceptible to mildew and were completely overgrown in three weeks to one month of incubation. Davis, Dreyfus and Holland<sup>5</sup> have employed a procedure for testing the mildew resistance of cotton goods similar to the one just described, with a period of incubation from 40 to 50 days. In experiments on mildewing "pure cloth" the following results, among others, are given:

"Seventh day.—Damp but nothing visible. Twelfth day.—Visible only under the microscope. Twentieth day.—Slight fructification. Twenty-eighth day.—Badly mildewed, brown spots, etc."

Their results, together with our observations, have convinced us that 30 days is the shortest allowable

period of incubation when testing fabrics for mildew resistance.

A serviceable test for mildew resistance of textiles should include the following factors:

- 1—Aërobic conditions of growth.
- 2—Proper humidity.
- 3—Proper temperature.
- 4—Subdued light.
- 5—Sufficient period of incubation.
- 6—Standard conditions with regard to the controllable factors involved in the test.
- 7—Simplicity of procedure.

To meet these conditions the following procedure has been adopted. Cut six discs about  $3\frac{1}{2}$  in. in diameter from the sample to be tested and place in running water at room temperature for at least 2 days. In the absence of running water place the discs in a beaker of water and change the water several times during the day. This soaking and washing is for the purpose of removing from the fabric as much of the water-soluble, germicidal and fungicidal substances as possible and also the fermentable material. If these are left in the fabric, they may suspend or hasten the development of the mildew spores, making it appear that the fabric is highly mildew-resistant or highly susceptible, whereas in practice the substances may be almost completely washed out by the first rain, and the resistance of the fabric become markedly different.

At the end of the period of soaking, place the discs between clean blotting papers or towels and remove excess of water by pressure. Place the discs in six bacteriological Petri plates containing 10 to 15 cc. of plain agar jelly free from nutrient matter, being careful that the plates do not become air-tight. The plates with the discs are incubated in a closed chamber at a temperature of 20° to 25° C. for 7 to 10 days. If they show a heavy and well-developed growth, the test is discontinued. If, however, the growth of mold is entirely absent or is merely starting, the discs are inoculated with stock cultures of *Alternaria*, *Cladosporium*, and a pink *Mucor*, and further incubated for from 3 to 4 weeks. The first period of incubation is designated for convenience as the "pre-inoculation period."

During the second period of incubation weekly examinations of the plates are made macroscopically and with the aid of the binocular microscope whenever necessary. The factors observed and taken into consideration, are:

- 1—Extent of contamination or so-called spontaneous growth.
- 2—Extent of inoculation growth.
- 3—Discoloration.
- 4—Strength of the fabric.
- 5—Nature of the predominating growth.

A rating on the basis of ten has been worked out which is, of course, arbitrary, and subject to future modification. Where results cannot be measured and expressed mathematically, precision cannot be expected. The definitions and ratings are based upon observable factors which do not lend themselves to definite measurement. They are, therefore, subject to errors introduced by the so-called individual equa-

<sup>1</sup> *Amst-und Anzeigeblatt für die Landwirtschaftlichen Vereine der Königl. Sachson*, 1854.

<sup>2</sup> *Beiträge zur Begründung einer rationellen Fütterung der Wiederkauer*, Braunschweig, 1860-4, 2 pts.

<sup>3</sup> *Z. biol.*, 21 (N. S. 3) (1885), 67-139.

<sup>4</sup> *Ann. Inst. Pasteur*, 25 (1911), 247-276.

<sup>5</sup> *Loc. cit.*, p. 205.

tion. However, after some experience, the worker obtains a concrete understanding of the terms "very heavy," "heavy," "considerable," "fair," and "negligible."

The rating is based on one month's incubation.

OBSERVATIONS				NOMEN- CLATURE
Contamination Growth	Inoculation Growth	Other Characteristics	RATING	
Very heavy <sup>1</sup>	.....	Tendering of cloth	0	Mildew - suscep- tible
Very heavy <sup>1</sup>	.....	Tendering not readily observable	1	Not mildew-re- sistant
Heavy <sup>1</sup>	.....	Marked discoloration	2	
Heavy <sup>1</sup>	.....	Visible discoloration	3	
Considerable	Fair	Slight discoloration	4	Negligibly mil- dew-resistant
Considerable	Negligible	No visible discoloration	5	Slightly mildew- resistant
Fair	Negligible	No visible discoloration	6	Considerably mil- dew-resistant
Negligible	Negligible	No visible discoloration	7	Mildew-resistant
Negligible	Visible only through binocular microscope	No discoloration	8	Highly mildew- resistant
Negligible	None	No discoloration	9	Very highly mil- dew-resistant
No	None	No discoloration	10	Mildew-proof

<sup>1</sup> Where the contamination growth is heavy the condition of the inoculation growth may be overlooked. In fact it is frequently overgrown by the spread of contamination molds.

Data permitting the comparison of the results of laboratory tests of the mildew resistance of textile fabrics by the above method with field exposures have been obtained, and, though at present still meager, are indicative of the value of the test. Pieces of treated and untreated cloth were stretched over frames in the vicinity of Washington for nearly a year. The samples were then brought into the laboratory and examined for mildew. The table shows the results of the laboratory test and outdoor exposure of some of the samples.

LABORATORY TEST				EXPOSURE TEST
NUM- BER	Contamination Growth	Inoculation Growth	Other Characteristics	
34791 <sup>1</sup>	Very heavy	.....	No readily observable tendering of cloth	Heavily mildewed
34792 <sup>1</sup>	Heavy	.....	Marked discoloration	Black mil- dew
34780 <sup>1</sup>	Heavy	.....	Marked discoloration	Black and yellow mildew
34772	Heavy	.....	Marked discoloration	Black and green mil- dew
34797	Heavy	.....	Marked discoloration	Consider- ably mil- dewed
34856	Heavy	.....	Marked discoloration	Black mil- dew
33309	Considerable	Fair	Slight discoloration	Some black mildew
34828	Considerable	Fair	Slight discoloration	Heavily mildewed
34832	Considerable	Fair	Slight discoloration	Mildewed
34834	Considerable	Fair	Slight discoloration	Mildewed
32409	Considerable	Negligible	No visible discoloration	Some black mildew
34826	Considerable	Negligible	No visible discoloration	Slightly mildewed
34748	Considerable	Negligible	No visible discoloration	Mildewed
33331	Fair	Negligible	No visible discoloration	No mildew
33460	Fair	Negligible	No visible discoloration	No mildew
32388	Negligible	Negligible	No visible discoloration	No mildew
33434	Negligible	Negligible	No visible discoloration	No mildew
32383	Negligible	Visible only through binocular microscope	No visible discoloration	No mildew
33017	Negligible	.....	No visible discoloration	No mildew
33001	None	None	No visible discoloration	No mildew
33003	None	None	No visible discoloration	No mildew

<sup>1</sup> The first three samples were of untreated gray duck—the remainder were from treated material.

It will be seen from these preliminary results that samples which by the laboratory method give a resistance of six or better withstood exposure for a whole year under normal weather conditions near Washington, D. C. How much longer these fabrics will

withstand exposure without mildewing is now being determined. The procedure can apparently be relied upon, especially in distinguishing between resistant and nonresistant treatments.

#### SUMMARY

I—The methods heretofore usually employed for testing mildew resistance of fabrics are outlined and their disadvantages pointed out.

II—A laboratory method is described which is simple in execution and the details of which have been standardized.

III—A rating on the scale of 10 and a system of nomenclature have been developed on the basis of laboratory observations. The practical significance of these underexposure conditions will be further studied and reported.

IV—A comparison has been made of the results of the laboratory test with results of exposure tests.

#### THE INFLUENCE OF THE METHOD OF MANUFACTURE ON THE USE OF CASEIN IN GLUE MAKING

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The urgent necessity for a water-resistant glue for use in aircraft construction was realized immediately upon our entry into the war, but at that time, in this country, relatively little was known regarding its preparation. The severe weather conditions to which airplanes are subjected and the impracticability of covering all glued joints in a machine with a waterproof coating, led the Air Service of the War Department and the Bureau of Construction and Repair of the Navy Department to adopt very exacting requirements as to water resistance for all glue used in the manufacture of certain aircraft parts. The U. S. Forest Products Laboratory, Madison, Wis., was called upon to investigate this subject in order to obtain definite information as to the properties of, and methods of obtaining water-resistant glue.

Two types of water-resistant<sup>1</sup> glue have been successfully developed, one based on soluble blood albumin and the other on casein. Casein is practically insoluble in water, but in the presence of alkaline substances it forms solutions which are highly viscous and possessed of marked mucilaginous properties. If lime is present, these solutions soon "set," and on drying form a hard mass which does not redissolve in water. Such a mixture of casein, lime and other alkaline substance, to which certain other ingredients may be added to confer additional desirable properties, forms the so-called "waterproof" casein glues which are commercially available at the present time.

In the early work at this laboratory in the development of casein glue formulas it was found that shipments of casein from different sources, or often two shipments from the same maker, exhibited such marked

<sup>1</sup> F. L. Browne, "Water-resistant Glues," *Chem. & Met. Eng.*, 21 (1919), 136.