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ABSORBENT PAPER PRODUCT AND PROCESS OF PRODUCING THE SAME

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1 Claim. (Cl. 92—40)

This invention relates to absorbent paper products and processes of producing the same, and it comprises an absorbent paper such as toweling, absorbent type toilet paper, blotters, and similar highly absorbent materials derived from wood pulp, and in which have been incorporated small amounts of added substances to preserve the paper against loss of absorbency; it further comprises processes wherein such preservatives are incorporated in the paper, for example by adding the substances to the beater, by spraying a solution of the preservative on the wet sheet as it leaves the wire of the paper machine but before it has been dried, or by spraying a solution of the preservative on the dried paper and again drying.

Paper toweling, absorbent type toilet papers, blotters and other paper products primarily used to absorb moisture differ from bond, writing, printing, and other substantially non-absorbent, or, at the most, superficially absorbent, paper. These differences are found in part in the actual manufacturing steps employed and also in the manner of cooking the pulp. Since absorbent papers must take up water rapidly, the beating and jordanning of the pulp are comparatively slight so that the pulp will not become to gelatinous and too much cut up. If the beating is prolonged, as for example in making bond paper, the resulting sheet is hard and the fibers are so closely associated as to preclude the use of such a felted sheet for paper toweling. In the manufacture of absorbent papers it is also desirable that the formation or structural relation of the fibers be as uneven and wild as possible, consistent with some strength, so as to increase both the rate of absorption and the absorptive capacity of the paper. Toweling is generally creped or embossed to further soften and break up fiber formation and thus increase absorption. The pulp is also somewhat more severely cooked than pulp used for making non-absorbent types of paper. This is to soften it and open up passages and holes in the fiber. It also thoroughly removes incrusting substances such as lignin and rosin, both of which tend to make the paper hard and less absorbent.

These differences in manufacturing operations are reflected in the physical properties of the paper. Paper toweling and blotters, for example, are unsized, and have surfaces which are highly porous and soft. Parchment, bond, writing, printing, and wrapping papers are relatively hard surfaced, lack marked porosity, and are filled and sized.

Present absorbent papers show greatly lessened absorbency after prolonged storage prior to use. One of the paper towels I have tested for absorbency lost as much as one-half of its ability to absorb water after six months storage. Another toweling showed a ninety percent loss in absorbency. Just why absorbent paper loses its initial high capacity for absorbing water is not entirely clear. I have, however, found that the loss bears no relation to changes in the strength, moisture, content, softness and flexibility of the paper. These qualities generally remain substantially the same during aging in storage although the paper may have lost from fifty to ninety percent of its capacity for absorbing water. My investigations have suggested that beta and gamma celluloses are involved in the matter. It is probable that these celluloses more or less generally form a coating on the fiber comprising the paper and that, on storage, these celluloses lose water by transference thereof to the alpha cellulose fiber in the paper. Loss of water converts the beta and gamma cellulose to a hard, dried, gel condition and, after such conversion, these forms of cellulose are not readily wetted again. The change is irreversible, in other words, loss of water from the beta and gamma celluloses converts them to irreversible gel form. That this is a reasonable explanation for the loss in absorbency is shown by the fact that paper which is very high in alpha cellulose does not develop the phenomenon of absorbency loss on storage. This is because a high alpha cellulose paper is substantially free of those beta and gamma celluloses which pass irreversibly to a hard, dried gel condition.

In order to determine the loss of absorbency on storage rapidly, and also to determine the effectiveness of the many "preservatives" against such loss which I shall hereinafter disclose, I can make use of a quick aging test. This consists in heating the paper in an oven at 100° C. for one hour. Absorbency is determined both before and after such accelerated aging, and this absorbency is measured by the time in seconds required for the paper to absorb one cubic centimeter of water. Paper toweling may also be tested for absorbency by determining its absorbency when freshly made, storing it for six months and then testing it again for absorbency.

For example, the following table illustrates the very great deterioration, or loss of absorbency, in ordinary bleached and unbleached paper toweling over six months.

Bleached towels

Absorbency when made (seconds)	Absorbency after 6 months storage (seconds)	Ratio of absorbency before and after storage
98	171	1 to 1.75
169	1700	1 to 10
274	925	1 to 3.37
193	886	1 to 4.6

Unbleached towels

240	645	1 to 2.68
457	2341	1 to 5.12
241	531	1 to 2.20
431	637	1 to 1.47
321	897	1 to 2.79
137	309	1 to 2.26

When making comparisons between various papers it is best to use the ratios of absorbency before and after storage as shown in the third column in the above tables.

The accelerated aging test described above is about equivalent to six months storage.

I have determined that this phenomenon of loss of absorbency is not due to oxidation. The loss develops even when the paper is subjected to accelerated aging in an atmosphere of pure nitrogen. The loss is also not due to a mere drying out of the paper, that is, removal of free moisture, for variations in the amount of free moisture due to partial drying out do not affect absorbency. Freshly made paper usually contains about 6 to 9 percent of free moisture.

It will thus be apparent that obscure reactions, some chemical, and others of a more physical nature, perhaps involving colloidal chemical phenomena, take place in the paper during storage. I have offered one reasonable explanation for the changes noted experimentally, but I do not, of course, wish to be bound by the theory presented above.

In the present invention, I have had for my object the discovery of some way of preventing this loss in absorbency; in other words I have endeavored to find ways of preserving all, or at least a large part of the normal capacity of freshly made paper for absorbing water.

I have now discovered that the addition of very small amounts of certain substances to the paper will inhibit loss of absorbency. This is, of course, in a sense a preservative action, but in the case of many substances I believe that the action is a sort of negative catalysis since it prevents what I believe to be a normal transference of water from beta and gamma cellulose to the alpha cellulose in the paper.

I have found that one of the very best groups of such preservative substances to add to the paper for this purpose are compounds commonly referred to as "wetting agents". These are generally sulfonated and sulfated organic compounds. Many of them go under trade names. A common one is Turkey red oil. Another is sulfonated neat's foot oil. In most instances the addition of as little as 0.2 percent, based on the weight of the paper, prevents all loss of absorbency over a period of six months or more. Such substances, when incorporated in the paper, produce no apparent change in its outward properties. Stiffness, softness, color, flexibility and tensile strength remain the same, although the latter may be reduced very slightly but cannot be detected except by the use of very accurate instruments. Occasionally the addition of the preservative may increase the absorbency somewhat. If the added substance be quite oily, it may soften the paper slightly and reduce its "rattle" but all of these changes are slight and inconsequential since I add such small quantities of wetting agents to the paper. My added substances function primarily to prevent loss of absorbency. They have little or no effect on any other properties of the paper.

Those substances which show the best preservative action, that is, the sulfonated and sulfated organic compounds, are not hygroscopic and do not noticeably change the normal moisture content of the paper. This shows that they do not function merely as water-holding substances to prevent a drying out action. Since they are effective in such small amounts I am led to believe that their action is a catalytic one as stated above.

Another class of substances which I have found to be effective, but which do not function in the same way as the wetting agents, are normally liquid polyhydric alcohols such as glycerine, glycol, and ethanolamine. These substances are hygroscopic. Greater quantities, of the order of 2 percent are necessary and this indicates a difference in the way the two groups act. I do not believe that these hygroscopic substances function merely by holding water in the absorbent paper, or by keeping it slightly moist. They may incidentally do this but I believe that they function chiefly by coating the fibers, thus retaining water in the beta and gamma celluloses. But this has nothing to do with the actual amount of uncombined water in the paper.

In addition to sulfonated oils and polyhydric alcohols, I have also found that certain alkaline-reacting inorganic salts such as borax, soda ash, and sodium sulfite will act as preservatives. This action appears to be quite specific. Neutral or acid salts show no preservative action, in fact they actually increase loss of absorbency. It is possible that the alkaline salt neutralizes any actual or potential acidity in the paper. This acidity, were it allowed to progress, would degrade the cellulose locally into beta and gamma cellulose and the latter would then lose water to form irreversible gels.

Of these three classes of compounds I find that the wetting agents are the best. The effectiveness of any particular preservative, or that of a substance thought to have preservative properties, can, however, be determined readily either by the accelerated aging test given above or by permitting the treated paper to age normally for six months or more.

The preservative can be incorporated in the paper in various ways. Perhaps the easiest way to test the effectiveness of any particular agent is to simply dip the towel or other absorbent paper in a dilute aqueous solution of the preservative and then allow the wet paper to dry in air. Hereinafter I shall describe various commercial methods of incorporating the preservative in the paper.

The following tables will illustrate the effectiveness of different wetting agents applied by dipping the paper toweling in a dilute aqueous solution of the preservative and allowing the towel to dry in air. In each instance, the dried,

treated towel contained 0.2 percent of preservative.

Bleached towels

Untreated—Ratio of absorbency when made to that after six months	Treated—Substance added	Ratio before and after six months
1 to 3.4	Neopen	1 to 1.12
1 to 3.4	Neomerpin SA. conc	1 to 1.04
1 to 3.4	N. S. L. neutral	1 to 1.56
1 to 2.88	N. S. L. acid	1 to 1.62
1 to 1.51	Nekal	1 to 1.0
1 to 3.4	Permeko	1 to 1.08
1 to 2.66	Gardinol	1 to 1.0
1 to 3.4	Green acid soap, L-1743	1 to 1.32

Unbleached towels

Untreated	Treated	
1 to 1.9	Neopen	1 to 1.21
1 to 1.9	Neomerpin SA. conc	1 to 1.05
1 to 1.9	N. S. L. neutral	1 to 1.41
1 to 1.9	N. S. L. acid	1 to 1.3
1 to 1.32	Nekal	1 to 1.1
1 to 1.4	Permeko	1 to 1.03
1 to 1.48	Gardinol	1 to 1.0
1 to 1.9	Green acid soap L-1743	1 to 1.44
1 to 3.61	Turkey red oil	1 to 1.06
1 to 3.61	Sulfo. neat's-foot oil	1 to 1.36

It will thus be noted that the addition of as little as 0.2 percent of Nekal to the toweling practically completely prevents loss of absorbency over a period of six months. The same paper unprotected would lose about fifty percent of its ability to absorb water.

About the same figures are obtained when Gardinol is used. As stated above, most of these wetting agents go by trade names. They are all sulfonated oils of various types and I usually use them in the form of their sodium or ammonium salts. Neopen is the trade name of a material produced by dry distilling rosin, treating the distillate with fuming sulfuric acid, and converting the sulfonic acid thus obtained to its sodium salt. Nekal and Neomerpin are the sodium salts of alkylated naphthalene sulfonic acid. Usually the alkyl group is isopropyl. Gardinol and Ocenol are the sodium or ammonium salts of alkyl sulfates of aliphatic alcohols of rather high molecular weight. In general these substances are all alkali metal salts of aliphatic or aromatic sulfonic acids or the alkali alkyl sulfates.

Sometimes soap is referred to as a "wetting agent" but this is in fact a misnomer. The term has a fairly restricted and definite meaning in the art and excludes common soap and other sodium salts of the simple higher fatty acids. As a matter of fact, soap is entirely unsuitable and increases loss of absorbency. One paper towel had, before treatment with soap, an absorbency ratio of 1 to 3.61. After incorporating 0.65 percent of soap and aging the absorbency ratio was 1 to 7.07.

I find that the manner in which the wetting agent is incorporated in the paper does not have very much effect on the preservative action. However, it has been found in the case of Neopen, one of the best to use, smaller amounts are required if a dilute solution of the agent is sprayed on the towel while the wet web is leaving the wire of the paper machine but before drying. Thus, as little as 0.05 percent of Neopen retained in the towel is sufficient to prevent aging to a satisfactory degree.

I have stated above that the normally liquid polyhydric alcohols are also effective. In the following table I have illustrated the results of tests on various alcohols of this class.

Bleached towels

Absorbency ratio without treatment	Alcohol	Percent	Ratio after treatment
1 to 3.4	Ethylene glycol	2	1 to 2.72
1 to 3.4	Diethylene glycol	2	1 to 2.48
1 to 3.4	Triethylene glycol	2	1 to 1.8
1 to 3.4	Triethanolamine	2	1 to 1.43
1 to 3.4	Glycerine	10	1 to 1.21

Unbleached towels

1 to 1.94	Ethylene glycol	2	1 to 1.34
1 to 1.94	Diethylene glycol	2	1 to 1.45
1 to 1.94	Triethylene glycol	2	1 to 1.49
1 to 1.94	Triethanolamine	2	1 to 1.63
1 to 1.94	Glycerine	10	1 to 1.79

But it will be noted that these substances are not as satisfactory for most purposes as the wetting agents.

The following table illustrates the effectiveness of various alkaline-reacting salts, the paper containing 2 percent.

Bleached towels

Absorbency ratio before treatment	Substance	Absorbency ratio after treatment
1 to 3.4	Na_2HPO_4	1 to 2.82
1 to 3.4	Borax	1 to 2.68
1 to 3.4	Na_2CO_3	1 to 2.09
1 to 2.55	Na_2SO_3	1 to 2.34

Unbleached towels

1 to 2.6	Na_2HPO_4	1 to 1.43
1 to 1.94	Borax	1 to 1.68
1 to 1.94	Na_2CO_3	1 to 1.15
1 to 1.94	Na_2SO_3	1 to 1.23

On the other hand, substances like aluminum sulfate, sodium sulfate and common salt actually increase loss of absorbency. The first two nearly double the loss and the sodium chlorid triples it.

If desired, two or more preservatives can of course be added to the paper. Usually only one is sufficient but in the interests of economy I sometimes find it advantageous to add a small amount of a more expensive preservative and augment its effect by including another less expensive agent.

When practising my invention commercially, I generally find it most advantageous to incorporate the preservative in the paper by simply spraying an aqueous solution of the preservative on the wet web of pulp after it leaves the wire of the paper machine but before drying. Alternatively, I can add the preservative, or a mixture thereof, to the beater and make the paper from the beaten pulp in the usual way, or the aqueous solution can be sprayed on freshly made dried paper and the paper re-dried. This is better than dipping the paper in an aqueous solution of the preservative but the dipping method can be practised. Other suitable ways can of course be employed. When using the wetting agents, I find it advantageous to spray the wet pulp with an aqueous solution usually containing up to about 5 percent of the agent. The exact concentration de-

pends upon the amount of water which can be conveniently sprayed and the amount of preservative to be applied. Generally a solution containing ½ to 1 or 2 percent of the preservative is best. Any alum in the paper, or added thereafter assists in fixing the preservative in the body of the paper.

It should be noted that this invention bears no similarity to the common addition of glycerine and glycol to ordinary non-absorbent papers. It is of course an old proposition to incorporate various amounts of hygroscopic polyhydric alcohols in printing and wrapping papers, vegetable parchment, and like hard-surfaced substantially non-porous products. This, however, is simply to keep the paper soft by preventing a physical drying out of the paper. It has nothing to do with the actual ability of the paper to absorb large quantities of water.

Similarly it is old to add small quantities of various alkalis to paper such as newsprint and it has even been suggested to incorporate Turkey red oil and naphthalene sulfonic acids to control the ability of printing papers to absorb coloring agents. In this case the added material is simply used as an ordinary wetting agent to promote absorption in a paper which is not readily absorbent for water. This is a common procedure when it is desired to color the paper with aqueous solutions of various dyes, etc.

But none of these prior processes deal with highly absorbent, unsized and usually unfilled papers and none of them are concerned with preventing loss of absorbency in such products.

Throughout this specification, and in the appended claim, I have used the words "highly absorbent paper" to denote paper products like paper toweling, absorbent type toilet paper, blotters and the like. I do not mean this language to include writing, bond, newsprint, wrapping, and like papers which are but very slightly absorbent, or superficially absorbent to a degree just sufficient to permit them to take up ink.

And by the term sulfonated organic material classed as a wetting agent, I mean to include sulphonic acids, alkyl sulphuric acids, and their water soluble salts such as the sodium and ammonium salts. I do not intend that this terminology shall include such substances as common soap.

Having thus described my invention, what I claim is:

The method of decreasing the normal loss of absorbency in unsized absorbent paper toweling when such toweling is stored for periods of six months or longer which consists in incorporating in the freshly-made toweling prior to storage thereof a small amount, of the order of .05 to 0.2 percent, based on the weight of the paper, of an organic material classed as a wetting agent and being chosen from the group consisting of sulfated and sulfonated oils, sulfonated rosin distillates, alkyl sulfates of higher alcohols, alkylated naphthalene sulfonic acids, and salts of these substances, said salts also being wetting agents, said paper towel containing the wetting agent displaying substantially no increase in absorbency when compared with paper toweling from the same stock but which does not contain said wetting agent.

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