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PERMANENT PAPER AND METHOD OF MAKING SAME

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This invention relates to paper and similar products composed of felted cellulosic fibers having improved permanence and stability on storage and heating. The invention includes the improved paper and other felted cellulosic material and methods of producing the same.

It is a well-known fact that articles composed of or containing felted or molded cellulosic fibers such as paper, board, wet-molded articles and the like lose much of their resiliency with the passage of time. It is also known that this development of brittleness is accelerated by heating; in fact, heating is a standard test method to determine the expected normal aging of paper products. The present invention has as a principal object the incorporation into paper of a class of materials which will reduce the development of brittleness in paper and paper articles, and thus increase their effective life.

It is also a known fact that paper and other felted fibrous articles containing acidic materials and normally having a pH of about 4 to 6 will deteriorate faster upon storage or heating than those which are completely neutral. For this reason the aging characteristics, for example, of ordinary writing paper sized with rosin size and alum are not ordinarily as good as those of unsized or untreated papers. It is a further advantage of the stabilizing agents of the present invention that they will retard the embrittlement and discoloration of paper containing small amounts of residual acid or of acidic materials.

Our invention is based on the discovery that ammonium and alkali metal salts of dicyanoguanidine are effective stabilizing agents to retard the deterioration of paper and other felted cellulosic products when incorporated therein in relatively small amounts, usually on the order of about 0.3% to about 10% by weight. We have found that the addition of relatively small amounts of these compounds to paper will prevent loss in tensile strength and in tear and fold resistance when the treated paper is subsequently aged and heated. Such improvements are achieved without simultaneously affecting the color and sizing properties of the paper. Inasmuch as the paper stabilizing agents of the above class are all substantially colorless and neutral in character, they do not alter the appearance or affect the utility of the paper for its intended purpose.

In practicing the process of our invention the ammonium or alkali metal salts of dicyanoguanidine may be added to the paper at any desired

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point during or after it is formed on a paper-making machine. Since all of the stabilizing agents are water-soluble they can be incorporated into the paper very simply by impregnation from water solution, and this can be done in conjunction with sizing agents and the like during the finishing of the paper if desired. Thus, for example, water solutions of our stabilizing agents may be sprayed on the felted paper sheet, or they may be applied as a tub size. When a closed white water system is used, they may be added to the paper stock suspension prior to formation of the sheet, and may be used along with other beater-sizing agents such as rosin size and alum, starch, glue, fillers, colors, resins and the like materials.

As is noted above, the minimum quantity of the stabilizing agents that will produce the desired result in paper are on the order of about 0.3%, based on the dry weight of the cellulose. For most purposes, satisfactory results are obtained when about 0.5% to about 5% of the stabilizing agent is used. Amounts of more than 10% usually produce no further advantages, and therefore are not recommended.

The ammonium and alkali metal salts of dicyanoguanidine, any of which may be used in practicing the invention, are all soluble in water but are normally solid and colorless and therefore do not change the appearance or ink-receiving properties of the paper. These dicyanoguanidine salts may be prepared by reacting alkali metal or ammonium salts of dicyandiamide with cyanogen chloride. The preparation of these salts is disclosed with particularity in U. S. Patent No. 2,371,100.

The invention will be further illustrated by the following specific examples. It should be understood, however, that although these examples may describe in detail certain specific embodiments of the invention, they are given primarily for purposes of illustration and the invention in its broader aspects is not limited thereto.

Example 1

A commercial sulfite bond paper was impregnated with a water solution of the stabilizing agents listed below by immersing the paper in a 1% of 5% aqueous solution thereof, draining off excess solution, and heating for one minute on a drum drier at 105° C. Samples of the impregnated paper were then subjected to the standard A. S. T. M. accelerated aging test by heating them in an oven at 103–105° C. for 72 hours. The unaged and aged paper, together with control samples, was then tested by the usual

physical methods. The results are given in the following table. In the headings of this table MD means "machine direction," CD means "cross direction" and Refl. means reflectance measured at 450 millimicrons on a G. E. recording spectrophotometer.

Stabilizer	Per Cent[1]	Unaged Paper			
		Sheet pH	M. I. T. Fold		Refl.
			MD	CD	
None (control)		5.4	87	33	72
Potassium Dicyanoguanidine	2.3	5.3	87	25	70
Sodium Dicyanoguanidine	2.1	5.4	85	28	71

Stabilizer	Per Cent[1]	Aged Paper					
		Sheet pH	M. I. T. Fold		Refl.	Percent Fold Retention	
			MD	CD		MD	CD
None (control)		4.9	35	22	67	40.2	66.2
Potassium Dicyanoguanidine	2.3	5.5	70	24	64	80.5	96
Sodium Dicyanoguanidine	2.1	5.6	69	24	64	75.3	85.7

[1] Means the per cent of retention of stabilizer, based on the weight of the cellulose.

Example 2

A safety-check base paper having a relatively low pH was impregnated, dried, and tested as in Example 1 with the following results:

Stabilizer	Per Cent[1]	Unaged Paper			
		Sheet pH	M. I. T. Fold		Refl.
			MD	CD	
None (control)		4.0	35	40	65
Potassium Dicyanoguanidine	1.6	4.8	23	26	66
Ammonium Dicyanoguanidine	1.4	4.4	21	24	66

Stabilizer	Per Cent[1]	Aged Paper					
		Sheet pH	M. I. T. Fold		Refl.	Percent Fold Retention	
			MD	CD		MD	CD
None (control)		3.8	2	4	59	5.7	10
Potassium Dicyanoguanidine	1.6	5.3	11	23	59	47.8	88.4
Ammonium Dicyanoguanidine	1.4	5.1	9	18	57	42.8	75

[1] Means the per cent of retention of stabilizer, based on the weight of the cellulose.

What we claim is:

1. Paper containing about 0.3 per cent to 10 per cent by weight of a member selected from the group consisting of ammonium and alkali metal salts of dicyanoguanidine.

2. A product according to claim 1 in which the paper is a normally acid paper having a pH of about 4 to 6.

3. Paper containing about 0.3 per cent to 10 per cent by weight of potassium dicyanoguanidine.

4. Paper containing about 0.3 per cent to 10 per cent by weight of ammonium dicyanoguanidine.

5. A method of improving the stability of paper against aging which comprises impregnating said paper with an aqueous solution of a member selected from the group consisting of ammonium and alkali metal salts of dicyanoguanidine and subsequently drying the paper to retain therein about 0.3 per cent to 10 per cent of said compound.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,371,100	Kaiser et al.	Mar. 6, 1945