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PAPER FOR GRAPHIC ARTS CONSISTING OF ASBESTOS FIBERS, ACRYLIC RESIN, AND SIZE

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ABSTRACT OF THE DISCLOSURE

An inorganic graphic art paper composed of asbestos fiber, acrylic resin binder and a non-coloring and non-fading hydrophobic size.

This invention relates to an improved paper for art work, and in particular comprises a novel inorganic paper for painting and other graphic arts having improved and permanent qualities and the method of manufacturing the same.

Common art papers or organic based materials utilized as a foundation for paintings and the like graphic arts exhibit several properties characteristic of their composition which are particularly undesirable and render them wanting in this service. The most pronounced and severe deficiency of typical cellulosic art papers is their innate property of discoloring or yellowing with age which in time detracts from or degrades the artists' colors or scheme thereof and the aesthetic properties and value of paintings and other graphic works. Moreover, cellulosic based or containing art papers are highly vulnerable to moisture conditions and changes, and the harmful effects thereof comprising the absorption and presence of water with the accompanying swelling and shrinkage and the attendant water content and dimensional changes of the paper substrate contribute materially to the degradation of the painting, etc. and accelerate its general deterioration through decay, mildew, etc. or differential in expansion and contraction of the phases, wrinkling, cracking, etc., all of which limit and reduce the effective life of the object. Furthermore, the affinity of cellulosic based papers, etc. for water and the consequential swelling results in cockling of art papers upon application of water paints or other water based agents.

It is a primary object of this invention to provide an art paper comprising a water and/or oil paint, and other graphic art foundation which is non-fading or of permanent brightness and whiteness, and is not susceptible to deterioration or change with age or upon exposure to other deleterious conditions such as actinic light, high humidities, or water, etc., whereby it constitutes an enduring and lasting material for paintings and drawings, photographs and any other type of graphic recordings.

It is also a primary object of this invention to provide a permanent graphic art paper having effective water resistance overcoming cockling and optimum rates of surface and internal water penetration enabling the application of water color paints with sharp, vividly discernible strokes and images or of non-feathering margins, and permitting the prompt washing off of water based paints to rectify mistakes or make changes.

It is a further object of this invention to provide a non-yellowing and permanent graphic art paper of improved and substantial dimensional stability, and of reduced swelling, shrinkage, wrinkle, curl and cockle due to humidity changes or moisture content.

It is a still further object of this invention to provide an inorganic paper which does not discolor or deteriorate

with age, has effective water and/or oil holdout permitting ample working periods and paints after their application, is free from cockling and proneness to movement due to changes in humidity or its water content and which is therefore readily adaptable for use in any of the graphic arts including painting with either water or oil colors, photographic prints, printed material or records wherein permanence in either service life or brightness is of paramount or of particular significance.

These and other objects and advantages of this invention will become more apparent from the hereinafter detailed description thereof.

This invention comprises an inorganic paper of maximum permanence and other effective and apt characteristics for the enduring and unchanging maintenance of paintings and photographs, printed entries, records, etc., which consists essentially of a particular combination of fibers, bond and size, each of specific properties, whereby their concerted effects provide a unique paper of improved receptivity for graphic art materials and lasting stability. Essentially the inorganic graphic art papers of this invention comprise, in approximate percentages by weight: 70 to 90% of a highly cleaned, fine chrysotile fiber having a surface area of about 18,000 to 22,000 square centimeters per gram; 8 to 15% of an acrylic resin binder; and 0.25 to 2% of a colorless or white hydrophobic size. Inorganic papers of this invention suitable for most graphic art service generally comprise those of the preferred compositions of, in percentages by weight: about 85 to 90% of the said chrysotile fiber, about 10 to 12% of the acrylic resin and about 0.5 to 1.0% of a transparent or white hydrophobic internal size.

The principal component of the inorganic graphic art paper of this invention consists of chrysotile fiber of a grade suitable for paper making, for example Group No. 5, refined to a fine condition of substantially all passing 14 mesh and highly cleaned as by the means of U.S. Patent No. 2,996,183 to Russum or a conventional cyclone cleaner. The fiber moreover must be well opened by a hammer mill, for example a vertical fixed arm hammer mill such as the Bauer Bros. Co. "Hurricane" pulverizer, or other apt fiberizing means to a majority of the fiber having a surface area of approximately 18,000 to 22,000 square centimeters per gram, and preferably about 20,000 square centimeters per gram.

The binder of acrylic resin imparts water resistance as well as serving to integrate the fibers into a coherent sheet of high strength and enduring properties. Acrylates which constitute white resins of high color stability are available in conveniently applicable water emulsion form for paper making stocks, and preferably should be selected from the higher melting point resins available to maintain rigidity or freedom from softening within the paper in use under all normal conditions. Apt water emulsion acrylic resins of high melting points are available under the Rhoplex trademark of the Rohm and Haas Company.

The sizing agent comprises hydrophobic sizing materials which are water dispersible, as for example in emulsion form, are colorless or white, and any oxidation products thereof are also colorless or white or they do not discolor under infrared or other actinic light. These include, for example, alkyl ketene dimers available from Hercules Powder Company under the trade name Aquapel, pine resin sizes which are light in color such as gum resins, silicones, light colored and non-fading soaps or saponified fatty acids, etc. Other common sizes such as starch, wax, bituminous materials or some resins such as wood resin either do not resist fading, yellowing or the like color deterioration, or impart dark or non-white coloring, or both, and as such are unsatisfactory for the purposes of this invention.

The sizing agents of this invention are preferably incorporated as an internal size, or wherein the sizing material is mixed into the slurry of the fibrous furnish at a suitable point or operation, such as the beater, prior to sheet formation whereby the sizing is relatively uniformly distributed throughout the fibrous body. Nevertheless, in lieu of, or in addition to the preferred internal sizing, a similar or like type of size material, for example, alkyl ketene dimer or silicone, can be subsequently applied as an aqueous or other apt solution or emulsion to the formed, partially dried paper sheet on the forming machine, for example, at the size press or on the calenders, providing a surface sized paper. In some cases, however, surface sizing has been noted to lower the brightness of the product and internal sizing through addition of this component at the beater is therefore generally more desirable.

The papers of this invention may, if appropriate, include minor quantities of ancillary ingredients to augment or introduce specific properties. These comprise fillers and a variety of typical agents, provided they do not introduce unwanted color or are susceptible to yellowing, fading or other changes degrading the brightness of the paper or in any way altering the basic properties of the product or functions of its respective essential constituents.

The permanent inorganic graphic art papers of this invention are in general produced from the aforedescribed asbestos fibers through the means of more or less conventional paper-making techniques and apparatus. For example, an aptly pulverized, opened and highly cleaned fiber is added to a beater or other wet refiner, preferably at lower than normal concentrations of 3% solids or less, and is further brushed out to eliminate clots. Next, the beaten composition is then diluted to approximately 0.25% solids and fed to a battery of centrifugal cleaners such as Dirtecs or Bauer cleaners wherein any remaining magnetic oxide of iron or heavy impurities is spun free from the fiber and discarded. To this cleaned, fine, opened fiber stock, a highly diluted acrylic resin emulsion of about 5% solids or less is added in amounts calibrated to provide the 8 to 15% of resin solids of the total final paper weight. The acrylic resin is thus deposited effectively on the fiber surfaces. If the hydrophobic size is to be

applied internally as is preferred, this size is now added to the stock slurry most effectively in aqueous emulsion form and in amounts designed to provide the 0.25 to 2.0% of the given size of the final paper weight. Also if foaming presents a problem, a small amount of anti-foaming agent may be added at this point. Finally a paper is formed from this stock in a conventional manner comprising the use of either a multicylinder machine or a Fourdrinier.

If the papers of this invention are to be employed as a foundation for oil paints or are likely to encounter other oily materials, its linseed paint base or other oil holdout property can be decidedly enhanced by a subsequent surface sizing, preferably in addition to the aforementioned preferred internal sizing, with an acrylic, silicone or the like substantially colorless, or white pigment filled, resin coating. Suitable surface coatings or sizings can be applied by any convenient common means following formation of the paper and is usually carried out with machine coating equipment. Size coatings for effective oil holdout comprise amounts or film thickness adequate to effectively seal the substrate without breaks or openings which, of course, in turn is dependent primarily upon the degree of smoothness or coarseness of the paper surface and its openness, and therefore must be designed to accommodate the given paper base. Suitable film thicknesses for good oil holdout on typical and relatively smooth inorganic papers of this invention comprise about 1 to 1.5 mils (0.1 to 0.5 lb. of solids per ream) with the amount proportionally increasing with the substrate coarseness.

When the papers of this invention are to be utilized as a base paper for photographic and the like prints they are also amenable to conventional sensitizing treatments and agents applicable to the particular system of reproduction of their designed use.

The permanent inorganic graphic art papers of the examples were formed on a standard multicylinder paper making machine from a dilute stock of less than about 1% solids comprising a fine, highly cleaned chrysotile fiber having an average fiber surface area of about 20,000 square centimeters per gram, an acrylic resin binder and the given hydrophobic internal size materials, each in the approximate relative proportions set forth in the tables.

TABLE 1.—COMPOSITION AND PHYSICAL PROPERTIES OF ASBESTOS ART PAPER

	Specifications	Example 1 Percent, dry	Example 1 Lb./beater, wet	Example 2 Percent, dry	Example 2 Lb./beater, wet
Furnish:					
Chrysotile Fiber		87.5	300	87.0	300
Acrylic Resin, solids (Rhoplex AC-61)		12.0	90	12.0	90
Hydrophobic size, solids (Aquapel 360)		0.5	15	1.0	30
Antifoam (Colloids 568)		.05	0.15	.05	0.15
			Data		Data
Physical Properties:					
Basis Weight, lb./100 ft.^{2}			4.7		4.8
Basis Weight, lb., 22" x 30" x 500 sheets			108		110
Thickness, mils	10–12		10.9		11.0
Density, lb./ft.^{3}			51.7		53.3
Mullen, p.s.i.			34		33
Tensile, lb./in.:					
MD [1]			24.0		23.1
CD [2]			22.6		22.4
Stretch, percent:					
MD			1.6		1.5
CD			2.2		2.2
Tensile, wet lb./in., MD			6.8		6.4
Tear, grams:					
MD			90		88
CD			97		97
Stiffness, grams:					
MD			1.3		1.3
CD			1.1		1.1
Gurley Densometer, sec./100 cc			432		424
Water Absorption, percent, 24 hr			67.1		70.5
Williams Water Penetration, grams:					
1 min	[3] 0.05		0.03		0.03
5 min	[3] 0.18		0.15		0.18
Organic, percent			14.9		14.8

[1] MD—Denotes machine direction or parallel to the web formation.
[2] CD—Denotes cross machine direction or perpendicular to web formation.
[3] Maximum.

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All pertinent properties of the papers of the examples of this invention are likewise set forth in the accompanying tables to fully demonstrate the unique and advantageous properties of the graphic art papers of this invention.

The water hold-out properties of the papers of this invention and of the examples were examined and evaluated by determining the water penetration upon the samples of the examples when measured as the weight of water taken up after 1 and 5 minutes of contact, with all materials at room temperature (70° F.), on a Williams penetrometer. The standards and degree of water hold-out of the products of the examples are reported as Williams Water Penetration.

The papers of these examples were unaffected after exposure for 100 hours in a Fade-O-Meter with the before and after brightness values unchanged whereas cellulosic based art papers became distinctly yellow.

The foregoing products of Examples 1 and 2 consisted of smooth surface papers. Graphic art papers and in particular those designed for water color paint applications are frequently embossed or heavily felt marked. The papers of the following Examples 3 to 6 comprise hand sheet products of typically embossed or heavily felt marked surfaces. Increased stiffness being a desirable characteristic in the rough surfaced papers, these examples include an optional technique comprising glass fiber fillers as a means of enhancing stiffness. The compositions and all essential properties of the papers of Examples 3 to 6 are all set forth in Table 2.

TABLE 2.—ASBESTOS ART PAPER HANDSHEETS

	Example			
	3	4	5	6
Sheet Set Furnish:				
Chrysotile Fiber	87	87	82	82
Acrylic Resin, solids (Rhoplex AC–61)	12	12	12	12
Hydrophobic Size, solids:				
(Aquapel 360)	1	-------	1	-------
(Hercules S 868)	-------	1	-------	1
Chopped Glass, ¼ in. long, 9 micron diameter	-------	-------	5	5
Physical Properties:				
Basis Weight, lb./100 ft.²	6.2	6.2	6.1	6.2
Thickness, mils	16	18	18	19
Density, lb./ft.³	46.3	40.9	41.0	38.9
Mullen, p.s.i.	52	48	58	55
Tensile, lb./in.	36.9	38.3	37.3	36.7
Stretch, percent	2.8	2.5	2.6	2.1
Tensile, lb./in., wet	11.5	14.6	11.5	10.8
Tear, grams	140	130	288	248
Gurley Stiffness, grams	3.5	3.6	3.7	4.3
Gurley Densomter, sec./100 cc.	420	370	330	330
Water Absorption, percent, 24 hr.	72	65	73	65
Williams Water Penetration, grams:				
1 min.	0.05	0.03	0.03	0.02
5 min.	0.15	0.15	0.13	0.12
Organic by Ash, percent	13.6	12.7	13.1	13.9
Fade-O-Meter Change, 50 hr.	None	None	None	None

Aquapel 360 is a Hercules Powder Company paper size consisting of alkyl ketene dimers and Hercules S 868 is a terpene, an unsaturated compound having the empirical formula $C_{10}H_{16}$.

EXAMPLE 7

An acrylic resin surface size, incorporating a typical white paper pigment blend, to introduce effective oil holdout to both smooth surfaced papers and embossed surfaced paper, as those of Examples 1 and 2, and 3 and 4, was formulated, in parts by weight, as follows:

Pigment blend

Kaolin clay	500.0
Titanium dioxide pigment	500.0
Surface active agent (Calgon)	3.0
Water	430.0
Sodium hydroxide	1.5

The foregoing pigment blend was ballmilled 16 hours,

then mixed with the acrylic surface size in the given proportions in parts by weight:

Pigment blend	143.5
Acrylic resin (Rhoplex B–15)	70.0
Water	30

1% Sodium hydroxide to pH 9.

The white pigmented, acrylic surface size was applied with a RDS Wire wrapped coating rod to the smooth surfaced papers in a double application to achieve a coating film of about 1 to 1.5 mils which provided good oil holdout. This coating was also applied to the embossed surfaced papers in amount designed to spread 0.2 to 0.5 lb. of surface size per 100 ft. square of paper and thereby effectively seal the surface introducing good oil holdout.

What we claim is:

1. A non-fading permanent inorganic paper for graphic arts consisting essentially of, in approximate percentages by weight: 70 to 90% of a highly cleaned chrysotile fiber having an average surface area of about 18,000 to 22,000 square centimeters per gram; 8 to 15% of acrylic resin; and 0.25 to 2% of non-coloring and non-fading hydrophobic size selected from the group consisting of alkyl ketene dimers, pine resins, silicones, soaps, and saponified fatty acids.

2. The non-fading permanent inorganic graphic art paper of claim **1** wherein the hydrophobic size comprises a surface size.

3. The non-fading permanent inorganic graphic art paper of claim **1** wherein the hydrophobic size comprises an internal size.

4. The non-fading permanent inorganic graphic art paper of claim **2** having a hydrophobic surface size selected from the group consisting of acrylic resins and silicones in amount of at least approximately 0.1 to 0.5 lbs. of resin solids per ream.

5. The non-fading permanent inorganic paper for graphic art of claim **1** consisting essentially of, in approximate percentages by weight: 80 to 90% of a fine, highly cleaned chrysotile fiber essentially all below 14 mesh and having an average surface area of about 20,000 square centimeters per gram; 10 to 12% of acrylic resin; and 0.5 to 1% of non-coloring and non-fading hydrophobic internal size selected from the group consisting of alkyl ketene dimers, pine resins, silicones, soaps, and saponified fatty acids.

6. The non-fading permanent inorganic graphic art paper of claim **5** having a hydrophobic surface size selected from a group consisting of acrylic resin and silicones in the amount of approximately 0.1 to 0.5 lb. of resin solids per ream.

7. A non-fading permanent inorganic graphic art paper of claim **5** wherein the non-coloring and non-fading hydrophobic internal size is selected from a group consisting of alkyl ketene dimers and pine resin.

8. The non-fading permanent inorganic graphic art paper of claim **5** consisting essentially of about 87% of chrysotile fiber having an average surface area of about 20,000 square centimeters per gram, about 12% of acrylic resin, and about 1% of alkyl ketene dimer size.

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