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2,964,403

SURFACE-SIZING OF FIBROUS VOID-CONTAINING SHEETS WITH HYDROUS ZIRCONIUM COMPOUNDS

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No Drawing. Filed Sept. 1, 1955, Ser. No. 532,125

9 Claims. (Cl. 96—75)

This invention relates to the surface-sizing of fibrous base material. The invention is particularly useful in making a photosensitive paper and will be first illustrated by description in connection with such use.

The art of making such photosensitive sheet including aluminum basic carbonate gel has been described in U.S. Patent No. 2,705,685, issued to John F. Cipriano on April 5, 1955.

We have now discovered a surface-sizing position and process for paper and like sheet material which serves to localize, on the surface of the sheet material, photosensitive chemicals or other aqueous compositions later applied thereto. The result is increased utility of the photosensitive composition, which gives clearer prints, for example, in use of the product in reproducing engineering drawings.

Briefly stated, our invention comprises the herein described process of and product resulting from applying, over a fibrous sheet, an aqueous dispersion of an adhesive and, suspended therein, a zirconium compound of special kind, the zirconium compound and adhesive being used in amount to fill voids at the surface of the paper but leave fibers of the sheet exposed between the voids after drying.

As to materials, the base to be sized is ordinarily paper as, for instance, mixed rag and wood pulp, or sulfite or sulfate pulp paper. In a modification we may use cotton, silk, rayon or other cloth including conventional fillers such as starch, clays, and the like.

As the zirconium compound, we use one that is hydrous, insoluble in water, and when suspended in finely divided form therein, is at least somewhat gelatinous. Examples of such zirconium compounds that meet the requirements and give the special results described herein are the hydrous hydroxide, basic carbonate, oxide, and basic phosphate, it being understood that the term "zirconium" as applied to the salts includes "zirconyl" and that the term "hydrous" as used herein means incompletely dried.

As the adhesive we use a water dispersible adhesive, the term "dispersible" including "water soluble." Examples of adhesives that illustrate the class and that we may use are glue, starch, emulsions of polyvinyl acetate, polyvinyl chloride and polyvinyl alcohol, and magnesium aluminum silicate known in the trade as Veegum.

As the photosensitive chemicals to be used, we employ any of those which are usual in making papers for copying engineering drawings, such as blueprint, brownprint, and positive white print papers. Examples of such photosensitive chemical compositions that illustrate the kind to be used are those including the combination of ferric salt and ferricyanide (this term includes ferric ferrocyanides), combinations of ferric salts and silver salts, and diazo intermediates with suitable coupling agents to form azo colors on exposure to light. These photosensitive materials may or may not include developers. The choice here depends upon whether the developer is necessary

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or, if necessary, is to be applied in making the photosensitive paper or applied later in a separate treatment.

Special advantages of our invention are obtained, for example, in the making of the so-called positive papers. In such papers, it is customary for large areas of the finished copy to be white instead of blue or other background color expected. Our zirconium and adhesive composition limits the penetration of the photosensitive chemicals and concentrates them on the surface of the paper. As a consequence, the exposure of the said chemicals is increased. There is decreased the proportion of unexposed chemicals which, if large, causes staining and discoloration of the background of the copy. The result of our process and composition is preservation in the finished copy of substantially the expected background color.

As to proportions, we use sufficient of the zirconium and adhesive compound mixture to form a continuous film over the fibrous sheet when wet at the time of application, but not enough to form a continuous film after the water has been evaporated therefrom. As a result we obtain a deposition of the zirconium and adhesive compound mixture in voids at the surface of the fibrous sheet without completely covering the fibers between the voids in the dried product. As the result, the fibers in the finished product remain exposed between the voids, to receive the photosensitive or other chemical applied later.

The numerical proportions of the zirconium and adhesive mixture to be used will vary with the kind of fibrous sheet material selected as a base. Using, for instance, a paper of composition half rag fiber and half wood pulp and of thickness 0.004", we applied 1 lb. of zirconium paste in treating both sides of 10 lbs. of the paper. This paste contained about 15% of zirconium compound calculated as ZrO_2 . Depending upon the paper thickness, the original size of the paper, and the absorptiveness, we may use zirconium compound calculated as oxide in the proportion of 0.5 part to 3 parts for 100 parts by weight of the paper. Ordinarily we use a higher proportion, within this range, when the paper is thin than when the paper is thick.

The adhesive is used in proportion to hold the zirconium compound deposited in the voids of the paper so as to prevent dustiness of the compound and also to aid in mordanting or bonding other materials applied to the paper or other fibrous base. Suitable proportions of adhesive are about 5-20 parts for 100 parts of the zirconium paste or 30-120 parts for 100 parts of the zirconium compound calculated as oxide.

As to conditions, we apply the zirconium compound and adhesive to the fibrous base material to be treated in any convenient manner, as by roller coating, immersion followed by squeeze rolling, or spraying on. In any case the equipment used is conventional.

We obtain particularly desirable results, in the retention of the zirconium compound and adhesive in the surface portion of the paper and localizing of later applied photosensitive material, when the fibrous base to which the zirconium compound and adhesive are applied is in dry condition at the start of the application. Thus we may apply our zirconium compound and adhesive in aqueous suspension and in paste form to paper that has been passed over some at least of the drying areas of paper manufacturing equipment. In fact, we ordinarily apply our zirconium compound and adhesive suspension either to paper between the first and last drying sections of the paper machine or to the finished completely dried paper.

The zirconium compound and adhesive paste are applied at a pH of about 6-7.5 and suitably at 6-6.5.

The invention will be further illustrated by description in connection with the following specific examples of the practice of it. In these examples and elsewhere herein

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proportions are expressed as parts by weight unless specifically stated to the contrary.

EXAMPLE 1

Water -----ml. 250
Veegum (magnesium silicate), HV grade -----g. 1
Carbonated hydrous zirconia -----g. 25

The materials are mixed and poured into a dish. Blueprint paper base is then floated over the material. The excess is scraped off by a round doctor blade and dried. Blueprint sensitized solution of any standard composition (here ferric salt and ferrocyanide) is then applied over the zirconium and adhesive sized paper, then dried.

Blueprints are then printed using commercial drawings and developed. The prints are very clear, sharp, and bright.

EXAMPLE 2

A mixture was made of 250 ml. of water, 1 g. of Ghatti gum as adhesive, and 25 g. of carbonated hydrous zirconia of zirconium content 16% calc. as the oxide. Paper was sized in the same manner as in Example 1, dried, and sensitized with blueprint chemical. The resulting blueprint showed a deeper blue background than the paper not sized with the zirconium and adhesive composition.

EXAMPLE 3

250 ml. of water, 1 g. of Veegum HV adhesive, 25 g. of carbonated hydrous zirconia and 1 g. of citric acid were mixed. Blueprint paper base was sized in the usual manner, dried, the blueprint sensitizing solution was applied, the whole dried again, and blueprints made. These blueprints showed darker blue backgrounds and sharper white lines than paper not sized with our treating composition.

EXAMPLE 4

The procedure of Examples 1-3 above is followed except that the carbonated hydrous zirconia (basic carbonate) there used is replaced by other hydrous zirconium compound, particularly the hydroxide, oxide, or basic phosphate, on an equivalent weight basis calculated from the zirconia content. These zirconia compounds are used in all cases in suspension in water.

The following examples illustrate the method of preparing the hydrous zirconia compounds for use in the composition and process here described.

EXAMPLE A

Preparation of carbonated hydrous zirconia gel

0.75 part of soda ash was dissolved in 152 parts of water at room temperature. A 10% solution of zirconium oxychloride was prepared by dissolving 2.2 parts of zirconium oxychloride $ZrOCl_2 \cdot 8H_2O$, containing 40% by weight of Zr calculated as ZrO_2 , in 19.8 parts of water at room temperature. The resulting zirconium oxychloride solution had a density of 7.35° B_é.

This latter solution was added to the soda ash solution at such a rate that approximately 20 minutes were required to add the total volume. Agitation was moderate. The pH which, at the beginning was slightly higher than 10, slowly dropped to approximately 5.1 at the end of the reaction.

The precipitated slurry was allowed to age for 30 minutes and was then pumped into a plate and frame filter press at approximately 45 lbs. pressure until no further liquid flowed from the filter press. The filter cakes were then washed with water until tests with $AgNO_3$ T.S. indicated minimum amount of soluble chlorides. The cake was a highly gelatinous white product. It was rendered homogeneous by mixing in a pony mixer. The product gave the following analysis:

Zirconium calc. as ZrO_2 -----percent. 5.0
Carbonate calc. as CO_2 -----do. 0.77
Chloride calc. as Cl -----do. 0.02
pH -----do. 6.6

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EXAMPLE B

Hydrous zirconia gel

32.6 parts of caustic soda were dissolved in 300 parts of water. 76.3 parts of zirconium sulfate, containing 32.8% of Zr calculated as ZrO_2 were dissolved in 2258 parts of water in a tank provided with an efficient type turbine agitator and equipped with radial baffles.

The sodium hydroxide solution was added to the zirconium sulfate solution at such a rate that approximately 60 minutes were required for the addition. The pH of the reaction mixture increased from a low of 1.4 at the beginning to approximately 6.1 at the end. The temperature during the reaction was maintained at 29° C.

The precipitated slurry was allowed to age for 1 hour after which it was filtered on a vacuum filter and washed free of soluble salts with water.

The resulting product was a white gelatinous material containing approximately 7.1% of Zr calculated as ZrO_2 .

It will be understood that it is intended to cover all changes and modifications of the examples of the invention herein chosen for the purpose of illustration which do not constitute departures from the spirit and scope of the invention.

What is claimed is:

1. A surface-sizing composition for sizing fibrous sheet material consisting essentially of an aqueous dispersion of a water-dispersible polymeric adhesive and an incompletely dried water-insoluble hydrous zirconium compound in gelatinous condition, the adhesive and zirconium compound being in the proportion of from 30 to 120 parts adhesive to each 100 parts of zirconium compound calculated as the oxide.

2. A surface-sizing composition in accordance with claim 1 in which the zirconium compound is hydrous zirconium oxide.

3. A surface-sizing composition in accordance with claim 1 in which the zirconium compound is hydrous zirconium carbonate.

4. A surface-sizing composition in accordance with claim 1 in which the adhesive is magnesium aluminum silicate.

5. A process of surface-sizing fibrous sheet material which comprises applying to a dry surface of the material a continuous film of the treating composition of claim 1, the film containing an amount of sizing material insufficient to form a continuous surface coating on the sheet, and then drying the film, whereby there is formed at the surface of the material a discontinuous surface size having fibers of the material exposed therebetween.

6. A process in accordance with claim 5 in which the fibrous sheet material is paper.

7. A process in accordance with claim 6 which comprises applying to the sized paper a photosensitive coating composition.

8. A surface-sized fibrous sheet material having a discontinuous surface size consisting essentially of a water-dispersible polymeric adhesive and a water-insoluble hydrous zirconium compound in the proportion of from 30 to 120 parts of adhesive to each 100 parts of the zirconium compound calculated as the oxide.

9. A photosensitive sheet comprising a surface-sized fibrous base in accordance with claim 8 and a photosensitive coating thereover.

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