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PRODUCTION OF ANTITARNISH WRAPPERS

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This invention relates to a process for the production of antitarnish paper and other wrappers. The tarnishing of silver and other metallic surfaces by hydrogen sulphide and other acidic compounds present in the atmosphere is well known. The problem is a serious one from a domestic and industrial point of view.

Many types of antitarnish wrappings have been proposed. Cloths and papers impregnated with various chemicals such as silver nitrate, sodium ferrocyanide, cadmium salts, aluminum sulphate, borax, zinc acetate, copper sulphate and many others are known, but none of the methods heretofore disclosed has presented an efficient and economic wrapper which is of pleasing appearance as regards colour and smell.

It is an object of our invention, therefore, to provide a method of imparting antitarnish properties to wrappings such as cloth, paper or other fibrous materials.

It is a further object of our invention to produce an antitarnish paper.

It is a further object of our invention to provide such a method that will require no large and costly equipment.

It is a still further object of our invention to provide such a method that will result in a cheap and efficient antitarnish wrapper.

It is yet another object of our invention to provide an antitarnish wrapper that will be pleasing in appearance, without any objectionable odour.

These and other advantageous objects are attained by the method of our invention as will be described hereinafter.

We have found that the disadvantages of previous methods can be overcome and a highly efficient antitarnish wrapper can be cheaply produced, by precipitating insoluble compounds of copper, lead, zinc or cadmium on the fibres of a fibrous material, or in a paper furnish. According to the method of our invention, the resultant material or paper contains the copper, lead, zinc or cadmium in finely divided insoluble form on its fibres, thus imparting the desired antitarnish properties to the wrapper.

Throughout the following examples, we have precipitated copper only on the wrapper fibres by the use of various copper salts. It is to be understood, however, that corresponding salts of lead, zinc and cadmium may be substituted. The results of the tests using copper are offered by way of illustration only, and are not to be construed as a limitation of the scope of our invention as defined in the claims appended hereto.

The precipitation of the copper on paper stock may be carried out in several ways. By our preferred method copper sulphate is added to the pulp in the beater or blending tank and is then precipitated on the fibres as the basic copper carbonate salt by the addition of sodium carbonate. The finished sheet has a characteristic pleasing pale blue colour which changes to a brownish black on exposure to hydrogen sulphide, thus indicating automatically when the antitarnish properties of the paper have been expended. The amount of copper added may

be varied within fairly wide limits depending upon the antitarnish capacity required in the finished paper. However, the presence of basic copper carbonate on the fibres reduces the strength of the finished sheet and in cases where strength is an important property it may be necessary to limit the amount of copper added. Our preferred range is from 0.1–4.0% copper, based on the weight of the paper, but for special purposes, percentages outside of this range may be used. In order to obtain as complete precipitation of the basic copper carbonate as possible, sufficient sodium carbonate should be added to raise the pH of the stock to a minimum value of 6.0. It may be desirable in some cases to raise the pH above 6.0, particularly where neutral or alkaline papers are required. Sizes or other additives which impart special properties may be incorporated into the sheet at any convenient stage during the process of manufacture.

In an alternative method for preparing antitarnish paper containing insoluble copper compounds, advantage is taken of the fact that copper forms insoluble compounds with certain sizing materials which in themselves impart desirable properties to the finished sheet.

In cases where a water repellant sheet is required, we prefer to prcipitate the copper as an insoluble salt of rosin acids. In this process the sodium salt of rosin, sold in the trade as rosin size, is added to the stock in the beater or blending tank. After thorough agitation copper sulphate is added in sufficient quantity to precipitate the rosin as insoluble copper rosinate. The finished sheet has a uniform pale green tint and has water repellant properties depending upon its content of copper rosinate. The amount of copper rosinate precipitated on the fibres may be varied over a fairly wide range, the limiting factor being the strength of the finished sheet, which decreases with increasing copper rosinate content. Our preferred range is from 0.5–5.0% rosin size, based on the weight of pulp, followed by sufficient copper sulphate to precipitate and fix the copper rosinate on the fibres.

In cases where the strength of the paper is an important consideration, we have found that the use of the insoluble copper salt of carboxymethyl cellulose as an antitarnish agent possesses certain advantages. The strength of a sheet containing copper carboxymethyl cellulose is superior to that of a similar sheet containing basic copper carbonate. Sodium carboxymethyl cellulose is added to the stock in the beater and at the completion of the beating cycle copper sulphate is added in sufficient quantity to precipitate the carboxymethyl cellulose. The amount of copper carboxymethyl cellulose present in the finished sheet may be varied over a wide range, but we prefer to use 1–5% sodium carboxymethyl cellulose based on the weight of the pulp and sufficient copper sulphate to precipitate the carboxymethyl cellulose as the copper salt.

The following description of experiments which have been performed by us will serve to illustrate the application of our invention. It is to be understood that our invention is not limited to the materials and conditions described in these experiments which are to be considered as examples only.

Example 1.—Illustrating the preparation of paper containing basic copper carbonate in finely divided form

360 grams purified pulp and 7.2 grams copper sulphate ($CuSO_4.5H_2O$) were placed in a laboratory beater containing 23 litres of water and beaten for 30 minutes under a 5.5 kilogram load. The resultant stock had a freeness of 585 ml. (Canadian Standard). 5.1 grams sodium carbonate was added to the stock which was then thoroughly agitated without load. The final pH was 7.5. Handsheets, prepared by Tappi Standard Method T205m–47, were uniformly pale blue in colour and had

a tensile strength of 22 lb. per inch. No copper was detected in the white water residual from the preparation of the handsheets, when determined colourimetrically by the potassium ferrocyanide method.

Example 2.—Illustrating the decontamination of air containing hydrogen sulphide by the use of tissue paper containing finely divided basic copper carbonate

25 grams of an 8 inch strip of 10 pound tissue paper, containing finely divided basic copper carbonate (0.56% copper based on the weight of the paper) was packed loosely in a glass tube (1¼ inches diameter by 3 feet long). 12 cubic feet of air, containing 0.027 gram hydrogen sulphide, were passed through the tube over a period of 2 hours and the exhaust air bubbled through an absorption tower containing ammoniacal cadmium chloride. Titration of the absorbing solution indicated the absence of hydrogen sulphide in the exhaust air.

Example 3.—Illustrating the decontamination of air containing sulphur dioxide by the use of tissue paper containing finely divided basic copper carbonate

25 grams of 10 pound tissue paper containing finely divided basic copper carbonate (0.56% copper based on the weight of the paper) was ground in a Wiley mill and then placed in a glass tube (1¼ inches diameter by 3 feet long). 100 cubic feet of air, containing 0.115 grams sulphur dioxide, were passed through the tube over a period of 17 hours and the exhaust air bubbled through an absorption tower containing a neutral solution of 2% hydrogen peroxide. Titration of the absorbing solution indicated the absence of sulphur dioxide in the exhaust air.

Example 4.—Determination of the capacity of paper containing finely divided basic copper carbonate for absorbing hydrogen sulphide

10 grams of a 10 lb. tissue paper, containing finely divided basic copper carbonate (0.56% copper based on the weight of the paper) was packed loosely in a glass tube as described in Example 2. 12 cu. ft. of air, containing 0.032 gram of hydrogen sulphide, were passed through the tube over a period of two hours and the exhaust air bubbled through an absorption tube containing ammoniacal cadmium chloride. At the conclusion of the experiment the absorbing solution was acidified and titrated with standard iodine solution to determine the amount of hydrogen sulphide absorbed. The absorbing solution was found to contain 0.012 gram hydrogen sulphide and 0.020 gram were therefore removed by the antitarnish paper. Since the copper present in the paper has a theoretical capacity for absorbing 0.030 gram hydrogen sulphide, the efficiency is calculated to be 67%.

Example 5.—Determination of the capacity of paper containing finely divided basic copper carbonate for absorbing sulphur dioxide

10 grams of a 10 lb. tissue paper, containing finely divided basic copper carbonate (0.56% copper based on the weight of the paper) were placed in an atmosphere of sulphur dioxide for 4 hours. The paper was removed, left standing in the air until the excess sulphur dioxide had escaped, then disintegrated in water and the sulphite content determined by titration with iodine. The paper was found to have absorbed 0.046 gram sulphur dioxide and thus the copper present had an efficiency of 82%.

Example 6.—Illustrating the antitarnish properties of tissue paper containing finely divided basic copper carbonate

A small piece of polished silver foil, 2" x 2", was loosely wrapped in 2 square feet of tissue paper (4.3 grams) containing finely divided basic copper carbonate (0.56% copper based on the weight of the paper). It was then placed in a jar of 0.25 cubic foot capacity

containing 0.0115 gram hydrogen sulphide, and left standing for 16 hours. At the end of this period no tarnishing was apparent. When unwrapped silver foil, or silver foil wrapped in ordinary tissue paper, was exposed in the same way to 0.0005 gram hydrogen sulphide, tarnishing was apparent after 1 hour.

Example 7.—Illustrating the preparation of tissue paper containing the finely divided copper salt of rosin acids

10 pounds of the sodium salt of rosin acids (rosin size) was added to 1000 pounds of purified pulp in 3500 gallons of water. The stock was then beaten in a Jordan refiner to a freeness of approximately 585 ml. (Canadian Standard). 21 pounds of copper sulphate ($CuSO_4.5H_2O$) was then added and the stock thoroughly agitated. The pH of the mixture was 6.0. It was converted to a 10 lb. tissue sheet, uniformly pale green in colour, on a standard cylinder machine. The tensile strength of the sheet was 140 grams per inch in the machine direction and the copper content was 0.16%. The capacity of this paper for absorbing hydrogen sulphide, as determined by the method given in Example 4, was 0.07 gram hydrogen sulphide per 10 grams of paper. The capacity for absorbing sulphur dioxide as determined by the method given in Example 5, was negligible.

Example 8.—Illustrating the preparation of paper containing the finely divided copper salt of carboxymethyl cellulose

360 grams purified pulp and 40 grams of crude hydrated sodium carboxymethyl cellulose (containing 10 grams dry weight high viscosity sodium carboxymethyl cellulose with a degree of substitution of 65%) were placed in a laboratory beater containing 23 litres and beaten for 30 minutes under a 5.5 kilogram load. The resultant stock had a freeness of 560 ml. (Canadian Standard). 15 grams copper sulphate ($CuSO_4.5H_2O$) was added to the stock which was then agitated without load. The final pH was 5.9. Handsheets, prepared by Tappi Standard Method T205m–47, were uniformly pale blue in colour and had a tensile strength of 23 lb. per sq. in. and a copper content of 0.18%. The capacity of this paper for absorbing hydrogen sulphide as determined by the method given in Example 4, was .0032 gram hydrogen sulphide per 10 grams of paper. The capacity for absorbing sulphur dioxide, as determined by the method given in Example 5, was negligible.

Example 9.—Illustrating the preparation of an antitarnish fabric containing finely divided basic copper carbonate

A strip of woven cotton fabric, weighing 3.9 ounces per square yard, was passed through a bath containing a 5% solution of copper sulphate. The excess solution was removed by means of squeeze rolls under light pressure and the fabric then passed through a 5% solution of sodium carbonate. The excess sodium carbonate solution was likewise removed by means of squeeze rolls and finally by washing thoroughly with water. After drying, the copper content of the fabric was 1.96% and its capacity for absorbing hydrogen sulphide, as determined by the method given in Example 4, was 0.072 gram hydrogen sulphide per 10 grams of fabric.

Example 10.—Illustrating the preparation of an antitarnish fabric containing the finely divided copper salt of rosin acids

A strip of woven cotton fabric, weighing 3.9 ounces per square yard, was passed through a bath containing a 3% solution of the sodium salt of rosin acids. The excess solution was removed by means of squeeze rolls under light pressure, and the fabric then passed through a 5% solution of copper sulphate. The excess copper sulphate solution was likewise removed by means of squeeze rolls and finally by washing thoroughly with

water. After drying, the copper content of the fabric was 0.29% and its capacity for absorbing hydrogen sulphide, as determined by the method given in Example 4, was 0.011 gram hydrogen sulphide per 10 grams of fabric.

Example 11.—Illustrating the preparation of an anti-tarnish fabric containing the finely divided copper salt of carboxymethyl cellulose

A strip of woven cotton fabric, weighing 3.9 ounces per square yard, was passed through a bath containing a 3% solution of sodium carboxymethyl cellulose (extra low viscosity, 65% substituted). The excess solution was removed by means of squeeze rolls, and the fabric then passed through a 5% solution of copper sulphate. The excess copper sulphate was likewise removed by means of squeeze rolls and finally by washing thoroughly with water. After drying, the copper content of the fabric was 0.57% and its capacity for absorbing hydrogen sulphide, as determined by the method given in Example 4, was 0.022 gram hydrogen sulphide per 10 grams of fabric.

Antitarnish wrappers may also be made from textile fabrics by the use of lead, zinc and cadmium salts. In such cases the insoluble compounds are precipitated on the fabric by a two stage process in which the fabric is first impregnated with a solution of a soluble salt of the metal and then with a solution of sodium carbonate.

In cases where it is desirable to size the fabric the insoluble salts of carboxymethyl cellulose or rosin acids may be applied. The fabric is first impregnated with the

solution of the sodium salt of carboxymethyl cellulose or the sodium salt of rosin acids and then with a solution of a soluble salt of one of the above mentioned metals.

It will be understood that we have described and shown the preferred forms of our invention, and that we may make such changes and alterations in the general arrangement and in the construction of minor details thereof as come within the scope of the appended claims without departing from the spirit of our invention and the principles involved.

What we claim as our invention is:

1. A process for imparting antitarnish properties to fibrous materials which comprises precipitating only finely divided basic copper carbonate on the fibres of the material.

2. A process for the manufacture of anti-tarnish paper which comprises adding a soluble copper salt to the pulp in the beater stage and precipitating only the insoluble basic copper carbonate upon the pulp fibres in a finely divided form by the addition of a soluble carbonate.

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