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PROCESS OF MANUFACTURING IDENTIFIABLE PAPER

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The invention described herein may be manufactured and used by or for the Government of the United States for governmental purposes without the payment to us of any royalty thereon, in accordance with the provisions of the act of April 30, 1928 (Ch. 460, 45 St. L. 467).

This invention relates to a process for manufacturing indentifiable paper, paper board or other cellulosic materials and to a means for distinguishing a portion of the cellulosic fibers thereof whereby they develop a distinctive color under chemical treatment, manipulation or reaction.

An object of this invention is the economic and efficient production of paper, paper boards and other cellulosic material which have incorporated therein cellulosic fibers chemically treated with inorganic chemical substances, compounds, or materials. A further object of this invention is the production of paper that may be used in Government bonds, legal documents, postage and revenue stamps, United States postal cards, visas, passports and the like for protection against counterfeiting. A further object and purpose of this invention is to make it possible for the identity or authenticity of a particular specimen of the paper, paperboard or other cellulosic material to be definitely determined; to identify or authenticate it as having been made in accordance with a particular formula or as being of a certain origin, or of a certain source of manufacture, notwithstanding the fact that the specimen under examination or test may have undergone considerable handling in commerce even to the point of near deterioration.

Identifiable paper, as heretofore manufactured for use generally as currency or bank note paper had incorporated therein short red and blue silk fibers as a means of identification. These silk fibers are visible to the naked eye and are of origin foreign to the cellulosic fibers from which the paper is fabricated. Identifiable paper has also been proposed wherein the mark of identification comprises fibers which are fluorescent under ultra violet light. We have found that by incorporating in paper a percentage of cellulosic fibers treated for the purpose of identification with certain inorganic chemical substances, such as ferric chloride or the combination of ferric chloride and tri-sodium phosphate, advantages result which are not obtainable with paper employing silk fibers or fluorescent fibers. One such advantage of employing fibers treated with inorganic substances, compounds or materials is that they are invisible within the paper structure to the naked eye, and do not reveal their presence to counterfeiters. Another advantage of employing such fibers over the silk fibers is that they are preferably identical with the untreated fibers comprising the entire sheet of paper, and do not therefore involve increased expense for material and labor.

Another advantage of employing fibers treated with inorganic chemical substances, compounds or materials as compared with fluorescent fibers is that the invention is practical for use in the field, without expensive ultra violet light equipment. The skill of a chemist or technician is not necessary, but a layman when properly instructed can detect the presence of the treated cellulose fibers by means of certain inorganic chemical reagents when applied to a particular specimen of the paper, paperboard or other cellulosic material, which immediately respond to such treatment by acquiring a color distinctive from that of the untreated fibers and from that which they and the untreated fibers previously had. Another advantage of the present invention is that unlike fluorescent fibers, the fibers treated with certain inorganic chemical substances, compounds, or materials cannot be destroyed in effectiveness by sunlight, bleaching agents, acids, alkalis, absorption of water, oil, gasoline, etc., and they therefore remain in the paper structure as a permanent means of identification.

The invention as herein described is particularly applicable to paper, this being a particular article of manufacture in which the utility of such a device is especially desirable, and in connection with which the invention has been tested on a production basis and found to be successful.

In accordance with our invention we form sheet cellulosic materials such as tissue, manifold, writing, bond, ledger, index, paperboard or other types of material from any suitable cellulosic fibers and incorporate in said cellulosic material a percentage of cellulosic fibers chemically treated with inorganic substances, compounds or materials of the same origin and production as the untreated fibers comprising the entire structure of the sheet.

The base material of the paper or other cellulosic article of manufacture may be any suitable stock employed in the fabrication of such cellulosic articles. For example, the paper or other cellulosic article may be manufactured from chemical pulp produced by the suphite, sulphate, or soda process from wood or from any chemical

pulp of vegetable or other origin. The paper or other cellulosic article may be fabricated or formed on the same machines and in same manner as such articles have been previously manufactured. For example, this invention is applicable to hand methods of making paper and cellulosic articles as well as to the usual well known modern machine methods of production. The paper or other cellulosic material may be of any suitable weight and thickness ranging from light weight tissue and manifold to the heavier weights of writing, bond, ledger, index and paperboard.

A description in detail of an illustrative instance of the practice of the invention follows:

Chemical wood pulp is disintegrated in the beater containing clear water held at a temperature preferably not exceeding 90 degrees Fahrenheit and kept at a consistency of about 1.5 percent. The beater roll is held in the raised position at all times, using it for circulation only. Commercial ferric chloride crystals also commonly known as 60 percent ferric chloride crystals dissolved in warm water to give a substantially 30 percent solution is added to the pulp suspension in the beater in amount constituting about 20 percent of the oven-dry weight of the pulp in the beater. Steam is turned on and the temperature of the pulp mix is raised to about 140 degrees Fahrenheit while the contents in the beater are circulating. As the pulp heats up it gradually becomes brown in color. The circulation of the pulp is continued for approximately 30 minutes at about 140 degrees Fahrenheit after which about two percent rosin size based upon the oven dry weight of the pulp is added. The concentration of the size solution when added to the contents in the beater must be 3 percent or less, and it should preferably be added across the beater just in front of the beater roll. No alum is needed. The beater contents consisting of the suspension of chemical wood pulp of about 1.5 percent consistency and about 2 percent rosin size based on the oven dry weight of the pulp, are now circulated for at least 5 minutes or until such time as it is considered that the rosin size has been well mixed into the pulp. The treated pulp suspension is diluted by filling the beater with cold water and the contents of the beater are circulated during the addition of the water to provide thorough mixing. The contents of the beater are dropped to a storage tank provided with a means for agitation and it is further diluted in the tank to a final consistency of about 0.7 percent. The treated fibers in the agitated storage tank are kept at about 0.7 percent consistency to permit accurate metering. The dilute stock is pumped continuously to a constant level over head stuff box and is metered through an adjustable gate to a pipe which conveys it to the mixing box of the paper machine. If a long pipe is used between gate and mixing box, additional dilution water may be introduced just after the gate to keep the treated stock flowing freely. The treated fibers are added at the mixing box in order to avoid all beating and jordaning action, which would shorten the fibers and might also loosen the adhering chemicals. Since a major requirement of this treated-fiber method of paper identification is maximum length of treated fibers, they are prepared without beating and they are added to the paper machine after all refining action has been completed. An added feature of the late point of addition is to provide as short a time as possible for the treated fibers to be mixed with the untreated paper stock before the paper is made.

We have found that for the purpose of our invention the chemically treated fibers may be produced involving a combination of ferric chloride and tri-sodium phosphate. This method is completely satisfactory and gives slightly different results which may be desired in some instances. It can be carried out at either low or high pulp concentration, but leads to a product in which there is no essential difference from that obtained with the ferric chloride alone. It requires more labor and greater attention. However, if a mill for any reason is unable to heat the pulp under treatment to the required temperature of about 140 degrees Fahrenheit, the use of tri-sodium phosphate might be necessary. In this instance it should be added in 15 percent solution after the ferric chloride has been heated with the pulp under treatment for 30 minutes with continual circulation in the beater. The amount of crystalline tri-sodium phosphate to use is twice the weight of the ferric chloride crystals. After the tri-sodium phosphate solution has mixed for about 10 minutes with the stock, 2 percent rosin size based on the weight of oven-dry pulp, at three percent concentration is added. The pulp is subsequently adjusted to pH 4.5 by the addition of alum.

Any suitable percentage of treated cellulose fibers may be mixed with the untreated cellulosic stock. For the purpose of our invention a suitable amount of treated cellulose fibers is 0.8 percent based on the weight of the dry cellulosic fiber comprising the finished paper. Obviously variations may be made, smaller or greater percentages of the treated fibers may be employed as desired.

As stated, this invention relates to the production of identifiable paper or other cellulosic material that is to be used for any purpose where identification is desirable or necessary and where the identifiable characteristics or the distinguishing characters of the paper or other cellulosic materials make possible the positive determination of their identity and authenticity or ready detection of counterfeit.

For an invention of this type to be of the desired practical value the method of practicing it must be simple, reliable and economical. That is, it should be capable of being performed quickly without complication of apparatus or of expert chemical technique. It must be reliable in the sense of giving results which are constantly reproducible under ordinary industrial conditions and under specifically prescribed procedure of examination or test.

This invention provides in the felted fabric of the finished paper or completed cellulosic product a percentage of permanent and invisible cellulosic fibers which have been treated with a ferric or ferrous compound alone, or in combination with a substance, such as a phosphate carbonate or hydroxide, with which it will unite to give an insoluble reaction product. Such treated fibers remain for any desired period during the marketing, industrial use and other life of the paper or cellulosic material, until by the application of suitable inorganic reagents, such as a soluble ferrocyanide followed by an acid they are rendered visible to the naked eye by individually acquiring a distinctive color aspect of permanent character. In the form of the invention herein described which is particularly useful where the attribute of secrecy is desired, the chemically treated invisible cellulose fibers do not affect the color, finish, formation, general appearance,

the feeling or other characteristics of the paper or cellulosic sheet in which they are incorporated and in which they are indistinguishable by physical or ordinary non-chemical methods of inspection or test. The fundamental principle in this particular method and the chemical materials involved as a means to establish the authenticity or identity of a particular specimen of the cellulosic product as here described, is that the treated fibers do not possess the property of acquiring a distinctive color by emitting a fluorescence when exposed to ultra violet light, but that the desired distinctive color of the individually treated fibers is produced by reaction of several chemical inorganic compounds upon the chemically treated cellulosic fibers. It will thus be perceived that the invention by which the foregoing results are attained consists in the case of paper, paperboard or other cellulosic products in providing chemically treated cellulosic fibers which react differently from the way in which the untreated fibers react, when all are together subjected to an examination or test treatment.

In any instance or at any time, days, months or even years after the manufacture of the paper or cellulosic material, or in any place however remote from factory or laboratory the invisible treated fibers may be made visible by application of certain chemical inorganic compounds by acquiring a desired distinctive and permanent color.

The particular method for producing color by chemical reaction in the illustration here given for the purpose of this invention, is the use of potassium ferrocyanide and orthophosphoric acid. The potassium ferrocyanide employed is recommended to be of reagent quality although cheaper grades of potassium ferrocyanide may serve as well. For example, a sample of commercial or technical grade potassium ferrocyanide was found to be fully satisfactory for the purpose of this invention. The orthophosphoric acid employed is of a quality conforming to the specifications of the United States Pharmacopoeia now in effect. Other grades such as Chemically Pure or Technical Quality may also be utilized if their purity is first established by test.

A thin film of 20 percent aqueous solution of potassium ferrocyanide is applied to the specimen of paper, paperboard or other cellulosic material under test or examination and then blotted to remove excess liquid. This treatment is then followed by application of a film of 53.6 percent orthophosphoric acid solution over the same area of the specimen and then again blotted to remove excess liquid. It will be observed that the ferrocyanide solution does not produce any color in the treated fibers even if permitted to remain on the specimen indefinitely. However, a few seconds after the application of the orthophosphoric acid solution, the treated fibers acquire a deep blue color.

In the present invention it is a unique feature that treatment of a percentage of the cellulosic fibers to be incorporated in the felted fabric of the paper, paperboard or other cellulosic material is accomplished by the fact that the ferric chloride in dilute solution under the effect of heat undergoes a hydrolysis to colloidal ferric hydroxide which carries an electrical charge opposite to that of the dispersed cellulosic fibers, and these components are thus attracted to each other, the insoluble ferric hydroxide depositing on and within the cellulosic fibers. When the first component of the test solution, that is, when the potassium ferrocyanide is applied to the specimen under examination or test, at any particular time, days, months or even years after the production of the paper or cellulosic sheet, it does not impart color, nor does it produce any visible change therein. However, when the first component is followed by the second component of the test solution, namely, by orthophosphoric acid, the fibers chemically treated with ferric chloride assume a deep blue color. This differential color effect between the chemically treated cellulosic fibers and the untreated cellulosic fibers would be impossible to duplicate without starting at the point of the formation of the paper, paperboard or other cellulosic material and then only when the formula and the percentages of the various components or of the inorganic chemicals in the treatment of the cellulosic fibers and in the testing of the specimen, are known.

While the invention disclosed herein may be applied to paper, paperboard or other cellulosic materials, it is to be understood that the foregoing detailed description is merely given by way of illustration and that the invention is not limited to that material nor to the exact method of production of the paper, paperboard or other cellulosic material, nor to the use of the exact inorganic chemical substances, compounds or reagents mentioned, nor to that method of application of the inorganic chemical reagents. Many variations may be made therein without departing from the intent or from the spirit of the invention.

Having described our invention it is intended that the patent shall cover by suitable expression in the appended claims whatever features of patentable novelty exist in the invention herein disclosed.

We claim:

1. The process of manufacturing identifiable paper which comprises forming an aqueous suspension of cellulosic fibers containing about 1.5 percent by weight cellulose, incorporating with said suspension about 20 percent by weight based on cellulosic content, of hydrated ferric chloride, hydrolyzing said ferric chloride and precipitating colloidal ferric hydroxide in said fibers by heating said suspension to a temperature of about 140 degrees F., then incorporating about 0.8 percent based on dry weight of the thus-treated fibers in a paper base stock, and then forming paper from the resulting mixed stock, whereby the resulting paper is latently identifiable.

2. In a process of manufacturing identifiable paper, the steps which comprise separately treating about 0.64 percent of the paper stock with about 0.16 percent of ferric chloride hexahydrate, hydrolyzing said ferric chloride to iron hydroxide whereby it is intimately bonded to said paper stock, and then incorporating the thus-treated stock with the remaining 99.2 percent of the stock and forming paper therefrom.

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