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PROCESS FOR THE MANUFACTURE OF SAFETY PAPER

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This invention relates to a process for the manufacture of safety paper.

So-called safety paper is used for documents of various kinds, for example cheques, for preventing falsification especially with the aid of chemical agents. It is necessary for such paper to give a distinctly visible reaction with acids, alkalis, oxidising agents and reducing agents. Consequently a number of different reagents must be added to the paper. This gives rise to difficulties when the reagents also react upon one another, so that the discolouration which is intended to indicate the falsification occurs prematurely. It is obvious that a safety paper of this nature would be useless.

Such difficulties can occur for example if the attempt be made simultaneously to incorporate in the paper a reagent which reacts with reducing agents and a reagent which reacts with acids, because reagents which are effective for indicating falsification effected with the use of reducing agents must be very sensitive, since forgers only use very mild reducing agents in order not to damage the paper itself.

Now the present invention relates more especially to a process which enables reagents which are sufficiently sensitive to reducing agents and reagents which are sensitive to acids to be added simultaneously to the paper pulp.

Known indicators for acids are certain metallic salts, for example iron cyanogen compounds such as manganese ferro-cyanide, copper ferrocyanide, or cobalt-ferrocyanide, which may be used either alone or in combination with iron salts. These compounds also give a reaction with oxidising agents. If an attempt be made to add these substances to a paper which contains, as the reagent sensitive to reducing agents, an inorganic salt for example which can be easily reduced to the metal, the later reaction with a reducing agent becomes impossible because the aforesaid salts and cyanides act prematurely on the inorganic salt and effect reduction.

The undesired reducing action of the acid indicators is due to the fact that directly they are introduced into the hollander they split off sufficient ions to effect reduction. The ion formation in the hollander as well as on the drying apparatus of the paper machine, where definite thermo-electrical processes take place, is promoted by the acidity of the pulp due to its content of alum which is necessary for sizing. Owing to this ion formation, the metal is separated from the inorganic salt which acts as the indicator for reducing agents either in the hollander or at the latest in the paper machine and premature discolouration of the material therefore occurs. Although, when the paper pulp has a neutral reaction, the formation of ions is only small, nevertheless the solubility product is still so great that the ions which are split off have sufficient reducing power. It must also be mentioned that the substances, for example the said iron cyanogen compounds, which are employed as indicators for acid are often contaminated by ionisable salts, for example iron salts, so that the number of free salt ions is thereby increased.

Also when the paper is stored discolouration can occur subsequently, since owing to the catalytic action of light and moisture decomposition and ion formation may occur in consequence of photolysis.

The aforesaid disadvantages are obviated by the process according to the present invention. The process of invention enables suitable metal compounds, for example iron salts or iron cyanogen salts which themselves have a strong reducing power, to be incorporated in the paper pulp as acid indicators together with easily reducible substances, for example easily reducible inorganic salts, without reduction of the inorganic salt being effected and discolouration of the paper being caused owing to separation of the metal.

In accordance with the invention, the metal compounds, for example iron salts or iron cyanogen salts which act as the acid indicators, are converted before or during their addition to the paper pulp or to the paper into only slightly dissociated, and in particular colourless or only slightly coloured complex salts of the metals of the sixth group of the periodic system which form acids or polyacids, for example into iron tungstate, ammonium-iron-cyan-tungstate or ammonium-iron-cyan-molybdate, or are mixed with buffering agents for example alkali metal salts of phosphoric or boric acid, which immediately take up ions occurring in the nascent state for example iron or cyanogen ions, and convert them into undissociated compounds.

It is known simultaneously to incorporate in safety papers indicators for acids and for oxidising agents, for example an iron salt and potassium-ferrocyanide as the acid indicator and manganese sulphate as the indicator for oxidising agents. In this case, however, the two different reagents do not react upon one another in the paper pulp. There is no question in this case of preventing any mutual reaction between the various reagents in the paper pulp or in the paper, though it was important in the known process

provisionally to separate the components of the acid reaction one from the other and to fix the corresponding metal precipitates on the fibres which was effected by means of resin compounds of the metal salts. This has nothing whatever to do with the present invention.

It is also known to effect a kind of buffering in order to protect the safety paper from external and atmospheric influences, for example by regulating the pH value of the finished paper to a definite value, so that the occurence of the discolouration which indicates the falsification can be determined. Finally an attempt has been made to prevent falsification by incorporating ink fixatives in the safety paper. In this case the ink fixative can again be protected by a stabilising agent. None of the known proposals however has been concerned in any way with enabling indicators for acids and for reducing agents to be incorporated simultaneously.

According to the first of the aforesaid methods of the invention, the iron or iron cyanogen molecule is converted into a colourless or only slightly coloured complex salt of a metal of the sixth group of the periodic system which forms acids or polyacids, for example tungsten. In these complex salts the iron or iron-cyanogen molecule is firmly joined to the central atom by a principal valency bond or by a residual valency bond. The complex salts are of surprising stability owing to their high molecular composition and are characterised by a very low power of dissociation. Further, if any slight dissociation should occur, the iron and the iron-cyanogen occur for the most part not as free ions but as complex ions, and no free ions having sufficient power prematurely to reduce the inorganic salt to the metal and thereby produce discolouration are therefore formed.

When paper which contains the iron or iron-cyanogen molecule in the form of these complex compounds is treated with acids, the complex compounds are frequently decomposed into the simple salts which possess a greater power of dissociation.

It frequently happens, however, that low molecular, highly coloured complex salts are formed by the action of acids on the colourless or only slightly coloured high molecular salts whereby a discolouration of the paper is produced.

According to the second of the aforesaid methods, an alkali metal salt, for example of phosphoric or boric acid is added, for example, to the iron or iron-cyanogen compound. The iron or iron-cyanogen ions which are in the nascent state are immediately taken up by these salts which act as stabilisers or buffering agents and are converted into insoluble compounds, the solubility product of which is so small that they cannot form sufficient free ions to be able to reduce the inorganic salt to the metal.

Example 1.—To the paper pulp in the hollander which contains an inorganic salt which is capable of being reduced to elemental form, for example mercury tungstate or barium tellurite or barium selenite, precipitated colloidal iron tungstate is added and the paper is impregnated with a solution of complex ammonium-iron-cyan-tungstate. The iron tungstate and ammonium iron-cyan-tungstate act in conjunction in the finished paper as an indicator for detecting acids.

Example 2.—The paper pulp which contains an inorganic salt which is capable of being reduced to elemental form is impregnated with a solution of ammonium iron-cyan-molybdate which acts as the indicator for detecting acids.

Example 3.—To the paper pulp in the hollander which contains an inorganic salt which is capable of being reduced to elemental form there is added precipitated colloidal iron tungstate and the paper is impregnated with a solution of potassium ferrocyanide which contains an alkali metal salt of phosphoric acid or boric acid as a buffering agent.

The paper pulp can also be impregnated only with alkali potassium-ferrocyanide solution to which an alkali metal salt of phosphoric acid or boric acid is added as a stabiliser.

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