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(54) **Cleaning pad for the removal of sulfates from frescoed surfaces.**

(57) Flexible coatings for the sulphation-removing cleaning of frescoed surfaces and for the cleaning thereof from residues of proteinic materials, in particular strengthening materials, comprising a fibrous support impregnated with a binding agent and with a mixture based on an anion-exchange material (e.g., an anion-exchange resin) and an aqueous solution of ammonium carbonate and/or bicarbonate.

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FLEXIBLE COATINGS FOR THE SULPHATION-REMOVING CLEANING OF FRESCOED SURFACES

The present invention relates to flexible coatings for the sulphation-removing cleaning of frescoed surfaces.

More particularly, the present invention relates to flexible coatings for the sulphation-removing cleaning of frescoed surfaces on plasters of prevailingly carbonatic nature.

It is known that works of art, such as frescoes and wall decorations in general, are subject to the action of such aggressive agents as SO_2, NO_x, CO_2, contained in the atmosphere in more and more dangerous amounts, or to the action of the inclemency of the weather, with consequent wall moisture, capillary transportation of soluble salts, fungus attacks, and so forth.

It is also known that one of the most dangerous forms of deterioration of the frescoed surfaces (and by "frescoes", the paintings are meant which are accomplished with water-dispersed paints on surfaces of fresh plaster made from lime putty and fine sand), is the one briefly defined as "sulphation".

It can be induced both by impurities of the mortars and of the inert substances used in them, by the wall constituents, by the action of salts carried by the capillary moisture, and by the combined action of the condensing moisture and of the sulphur dioxide contained in the atmospheric air.

This ill-famed phenomenon can also cause the complete loss of considerably interesting works of art.

In fact, the transformation of calcium carbonate, which constitutes the colour binding agent in the real frescoes, into calcium sulphate dihydrate (sulphation) involves a considerable increase in specific volume of the mass, with the consequent arising of stresses, growth of needle-like or lamellar crystals.

All of the above causes in the painted layer liftings, scalings, loosenings and formations of patinas with the consequent loss of cohesion.

Furthermore, should the sulphated surface come into contact with water, the not negligible solubility of calcium sulphate dihydrate would cause the irretriavable loss thereof.

The actions of recovery and preservation of the pictorial works of art concern the difficult activity simply known as "restorations".

One of the must used remedies for that purpose, prior to the advent of the synthetic materials, consisted in fighting the scaling of the pictorial layer by means of strengthening agents of more or less secret formulations, in any case with a prevailingly proteinic base: egg, animal glues, and so forth.

But the ageing of these strengthening agents has always led to impressive phenomena of frescoes veiling, in the form of dark patinas, with the consequent loss of chromatism and legibility of the work of art.

The present trend of carrying out restorative operations only after an exhaustive preliminary analytical work, and with supporting scientific activities, has made it possible to develop restoration techniques more consistent with the present needs, and controllable both in their effects and in their action.

A classic method for removing the sulphation consists in acting on it with ammonium carbonate solutions, according to such modalities as not to endanger the integrity of the work of art, and in such a way as to restore a carbonatic surface, with the sulphate ion being removed as ammonium sulphate, by means of a double-exchange reaction.

For the purpose of preventing a re-sulphation of other carbonatic areas by the ammonium sulphate, a subsequent treatment with barium hydroxide solutions is carried out, which causes a sulphate to be formed, having a low specific volume, and a high chemical inertness.

Furthermore, the excess of barium hydroxide can turn again into barium carbonate, contributing to strengthen the plaster.

Furthermore, other formulates endowed performing a sulphation-removing and cleaning action are known, and approved by the various authorities and bodies entrusted with the protection of the artistic and cultural goods; to them the well-known B57 belongs, whose action is essentially based on the combined action of ammonium carbonate, and of salts and detergent compounds in aqueous solution.

Said formulates are carefully applied and removal by sponging and other delicate mechanical actions after rigorously controlled times of contact with the surfaces.

It is furthermore known that in the preliminary operations of chemical analyses, regularly carried out before the restoration interventions, the need arises for the intensity of the sulphation of the surfaces of the frescoes to be verified and possibly determined.

The above can be qualitatively made by means of contact reactions or quantitative measurements can be carried out, after drawing samples which, due to reasons of integrity of the work of art, can never assume dimensions representative of the surfaces to be examined.

The Italian patent application No. 21,706 A/85 has proposed compositions for the sulphation-removing cleaning and the analysis of the sulphation

of frescoes surfaces comprising a mixture, generally having a paste form, of an aqueous solution of ammonium carbonate with an anion-exchange resin in powder form.

But in the application of these compositions some problems can occur, which make their use difficult or laborious.

For example, in the contact cleaning of frescoed plasters, the granulometry of the ion-exchange materials must be carefully selected so to minimize their penetration into the microcavities and surface interstices.

That need generally causes the increase of the particle size of the ion-exchange materials, with a consequent loss of effectiveness of the treatment, caused by a reduction in the contact surface areas.

Furthermore, the not particularly small particle dimensions have a negative influence on the characteristics of spreadability and self-support of the paste-like mixtures, of not suitable consistency for the sulphation-removing treatments.

Thus, it becomes often necessary to interpose, between the frescoed plaster and the sulphation-removing paste, a protective layer, such as, e.g., of light paper, non-woven fabrics, etc., with the effectiveness of the ion exchange being furthermore impaired, and/or to support the same paste by means of suitable gauze fabrics, non-woven fabrics, filter papers, and the like.

The Applicant has found now that the above mentioned drawbacks can be overcome by means of flexible coatings for the sulphation-removing cleaning of frescoed surfaces which, when applied to plaster surfaces of prevailingly carbonatic nature, make it possible to perform in an easy and quick way, without any risks for the integrity of the paint, the following operations:

-quantitative determination of the degree of sulphation of the surfaces;

-removal of the sulphation;

-cleaning of the surfaces for strengthening materials of proteinic nature.

The object of the present invention are therefore flexible coatings for the sulphation-removing cleaning of frescoed surfaces of prevailingly carbonatic nature comprising a fibrous support impregnated with a binding agent and with a paste-like mixture, comprising an aqueous solution of ammonium carbonate and/or bicarbonate and by an anion-exchange material in powder form.

Examples of fibrous supports suitable for preparing the flexible coatings of the present invention comprise the filter papers, the papers endowed with high enough wet-resistance, the so-said dry-papers, i.e, those papers which are prepared from cellulose fibres and synthetic binding agents, cellulosic non-woven fabrics with or without synthetic fibres, woven fabrics endowed with the proper compactness, flexibility and hydrophily, of natural and/or synthetic fibres, such as wool, cotton, flax, jute, acrylic fibres, polyester fibres, polyolefinic fibres, and so forth.

The anion-exchange material, of both weak and strong type, contains preferably the activated functional groups, e.g., in the form of aminic groups or quaternary ammonium bases, free, or salified, and particle dimensions preferably lower than 0.1 mm.

Examples of suitable anion-exchange materials are supplied by the anion-exchange synthetic resins, provided with basic functional groups, in particular, the resins with a matrix based on polymers or copolymers of styrene, of acrylic monomers or on polycondensation resins, or also on crosslinked and functionalized polysaccharides.

The weight ratio of the anion-exchange material to the solution of ammonium carbonate and/or bicarbonate is comprised within the range of from 0.5 to 3.

Suitable concentrations of the solutions of ammonium carbonate and/or bicarbonate have resulted to be those comprised within the range of from 1 to 20% by weight; this does not however constitute a limitation.

Such concentrations can be varied by successive approximations, sticking more to the criteria of extreme prudence which must guide the operations on works of art, rather than to the stoichiometric requirements.

Suitable binding agents which can be used in the preparation of the flexible coatings of the present invention comprise the aqueous dispersions of synthetic polymers and/or copolymers with particle charge compatible with that of the necessary anion-exchange materials. For that purpose, acetovinylic binding agents, e.g., the ethylene-vinyl acetate (EVA) copolymers in practically non-ionic dispersion, can be used, as well as polyurethanic binding agents always in non-ionic characteristics dispersion, with concentrations of the latexes comprised within the range of from 20 to 50% by weight, optionally the binding agents comprise co-binding agents, also anionic, such as, e.g., the salified polymers of acrylic and/or methacrylic acid, in the form of ammonium salts.

Useful additives for obtaining pastes suitable for coating the fibrous supports, can be the kaolinites, the attapulgites, the clay materials in general, with a sufficiently fine granulometry and with a high water retention, at concentrations around 20% by weight relatively to the fine exchange-resin. Useful dimensions have demonstrated to be those equal to, or lower than, 100 micrometres; this is not, however, a limitative criterion.

These mineral additives can be useful for improving the rheologic behaviour of the paste and

make it possible a more regular application thereof.

Also surface-active compounds, both of non-ionic and cationic type, can result useful, for improving the wettability of the components, as well as the germicidal compounds, from quaternary ammonium bases, in the amounts which are regarded as being the most suitable.

The impregnation of the fibrous support can be accomplished by means of known techniques, such as, e.g., by means of spreading means, brushes, palette-knives, doctors, rollers, spraying equipment, etc., with the desired amounts being deposited.

The so-obtained coating is dried and exsiccated at a mild temperature, generally not higher than 50°C, and is stored for long time periods.

When the coating is used, it is reconditioned, e.g., by dipping in demineralized water, or in suitable solutions of ammonium carbonate and/or bicarbonate, and is directly applied into contact, from the ion-exchange material side, with the frescoed surface to be treated, thus all of the problems being overcome, which derive from the use of materials having a consistency and rheological characteristics unsuitable for obtaining self-supporting preparates.

After the use, the flexible coating of the present invention can be used again for sulphation-removing treatments, after a preliminary reactivation by digestion in regenerating solutions, such as, e.g., the ammonium carbonate and/or bicarbonate solutions may be, until the physical-mechanical characteristics of the same coating allow so doing.

Due to the delicacy of the uses of the coating of the invention, e.g., on frescoed surfaces of considerable artistic interest, a preliminary washing thereof in a stream of demineralized water is recommended; in this way, bringing undesired substances into contact with the surface to be treated is prevented in the most absolute way.

According to a further practical embodiment, the flexible coating of the present invention can be obtained by impregnating the fibrous support with a paste of an anion-exchange material in powder form and water, and a binding agent.

The impregnated support is dried and exsiccated at a mild temperature, generally not higher than 50°C, and is stored for long time periods.

When the coating is used, it can be reconditioned by means of demineralized water, or in suitable aqueous solutions of ammonium carbonate and/or bicarbonate, with concentrations comprised, e.g., within the range of from 1 to 20% by weight.

The reconditioning in demineralized water can be necessary in case of treatments of particularly deteriorated frescoed surfaces, so that it is preferable to operate with low-aggressivity coatings. That means eliminating the ammonium salt and operating in the presence of the anion-exchange material only.

The flexible coating of the present invention performs its action in the presence of aqueous phase, so, it could be useful, for some applications, to slow down the exsiccation rate thereof, by means of sheets of plastic films, or supplying water or carbonate-containing solution by means of pads or imbibition by capillarity.

The considerable stability of the preparate and the total absence of secondary effects due to the release of undesired substances, makes it possible, in principle, to treat a surface for an unlimited number of times.

Useful modifications which do not endanger the originality of the invention are:

-variations in granulometry and in type of exchange materials;

-variations in the ratio of the anion-exchange material to the ammonium carbonate and/or bicarbonate solution;

-variations in concentration of ammonium carbonate and/or bicarbonate;

-use of detergent, non-ionic or cationic surface-active agents with also germicidal action.

Such modifications can be necessary in that a frescoed surface generally poses problems, as to the restoration operative procedures, which are different from point to point.

The following Examples illustrate the present invention without however limiting it.

Example 1

A preparate, obtained according to the following modalities and composition, was spread on dry-paper of approximately 45 g/m^2, with the aid of a brush. After drying and exsiccation the coating deposit resulted equal to an average of approximately 70 g/m^2.

The modalities of preparation of the preparate are:

To 100 parts of weak anion-exchange resin Kastel A101 by DOW CHEM., in the form of a fine powder with the fraction finer than 0.053 mm constituting more than 95% of its weight, 10 parts were added of an aqueous solution at 25 % of an anionic surfactant, of the ethoxylated alkyl-phenol type; they were then wetted with 175 parts of demineralized water.

Separately, the following ingredients are prepared and mixed with one another: 75 parts of acetovinylic (EVA) latex Vinnapas EP14 by WACKER, 75 parts of demineralized water, 4 parts of an acidic acrylic latex Crilat D159 by VINAVIL, 80 parts of a 15% solution of ammonium carbonate; this formulation is added, with suitable stirring, to the paste of water and anion-exchange resin.

After minor adjustments in consistency, the preparate was applied to the above said support by means of a brush.

The obtained coating, after exsiccation, was washed in a stream of demineralized water and was conditioned in a 7% ammonium carbonate solution.

By a high-flexibility and wet-resistance supported anion-exchange material being thus become available, it was possible to apply it, making it perfectly adhere, to a frescoed surface of Brancacci chapel in Florence. The treated surface portion, which had, before the treatment, a sulphation level of about 5 g of $SO_4^=/m^2$, showed, after the end of the treatment, a practically negligible sulphation degree.

Example 2

Two layers of a preparate, obtained according to the following modalities were applied, by brush, on dry-paper of about 45 g/m² and on cotton cloths of about 100 g/m² of weight.

After drying and exsiccation, the coating deposits were respectively of about 110 and 140 g/m².

Modalities of preparation of the preparate:

To 100 parts of weak anion-exchange resin Kastel A101 by DOW CHEM., in the form of a fine powder with a content of fraction finer than 0.053 mm higher than 95% of its weight, 17 parts of attapulgite, type Attapulugs clay 100/up by ENGELHARD and 200 parts of an 0.3% solution of benzyltrimethylammonium chloride are added, and the whole mass is homogenized.

Separately, the following ingredients are prepared by mixing, in the order: 75 parts of acetovinylic (EVA) latex Vinnapas EP14 by WACKER, 80 parts of demineralized water, 4 parts of a 15% solution of ammonium carbonate; this formulation is added, with suitable stirring, to the paste of water and anion-exchange resin.

The coatings on the basis of supported anion-exchange material, obtained as said above, were dried, washed in a stream of demineralized water, and conditioned in 7% ammonium carbonate solutions.

They were easily applied to different treatment situations, and on different materials, in any case a good sulphation-removing effect being obtained, which was easily documented by X-ray fluorescence analysis carried out on coatings of the invention removed from the treated surfaces.

For example, by means of one application only, under free-evaporation conditions, the sulphation was removed from a portion of the frescoed surface of the Brancacci chapel of Florence, together with the proteinic substances with which the same surfaces had been treated on the occasion of prior restorations. The degree of sulphation of the surface was of about 5 g of $SO_4^=/m^2$.

Example 3

A preparate, obtained according to the following modalities was applied, by palette-knife, on dry-paper of about 45 g/m².

After drying and exsiccation, the coating deposits were of the order of 80 g/m² on the average.

Modalities of preparation of the preparate:

To 100 parts of strong anion-exchange resin, OH form, Kastel A500N by DOW CHEM., in the form of a fine powder with a content of fraction finer than 0.1 mm higher than 85% of its weight, 17 parts of Attapulugs clay 100/up by ENGELHARD, and 200 parts of an 0.3% solution of benzyltrimethylammonium chloride are added. After homogenization, 77 parts of aqueous polyurethanic dispersion Purbinder N73 by ROL S.p.A., previously diluted with 67 parts of demineralized water, are added. The obtained paste resulted quite well applicable by palette-knife, to outstretched, damp sheets of dry-paper.

The coating on the basis of supported anion-exchange material was submitted, after drying, to a washing in a stream of demineralized water, and a part thereof was then conditioned in a 12% ammonium carbonate solutions.

The so obtained coatings showed a considerable sulphation-removing effect on portions of the frescoed surface of the Brancacci chapel of Florence having a degree of sulphation comprised within the range of from 4 to 5 g of $SO_4^=/m^2$.

Example 4

On a wet-resistant filter paper , of the weight of 40 g/m², the preparate having the hereunder reported formulation was spread by means of a brush:

100 parts of weak anion-exchange resin Kastel A101 (DOW CHEM.), in the form of a fine powder (>95% smaller than 0.053 mm);

65 parts of acetovinylic (EVA) latex, Vinnapas EP400 by WACKER;

225 parts of demineralized water.

The application of a single layer made is possible to obtain a deposit of dry preparate around 40 g/m².

The coating of the invention, after washing in a stream of demineralized water, and conditioning in a 5% solution of ammonium carbonate, was applied both on a surface of sulphonated limestone,

and on a frescoed surface of 1400. In both cases, it was possible to document cleaning and sulphation-removing effects, by means of visual inspections and chemical analyses.

Claims

1. Flexible coatings for the sulphation-removing cleaning of frescoed surfaces of prevailingly carbonatic nature comprising a fibrous support impregnated with a binding agent and with a paste comprising an aqueous solution of ammonium carbonate and/or bicarbonate, and an anion-exchange material in powder form.

2. Coatings according to claim 1, wherein the fibrous support comprise the wet-resistant filter papers, the dry-papers, cellulosic non-woven fabrics with or without synthetic fibres, woven fabrics of natural and/or synthetic fibres, such as cotton, flax, jute, acrylic fibres, polyester fibres, polyolefinic fibres.

3. Coatings according to claims 1 or 2, wherein the anion-exchange material is a synthetic anion-exchange resin, with a particle size lower than 0.1 mm.

4. Coatings according to any of the preceding claims, wherein the weight ratio of the anion-exchange material to the ammonium carbonate and/or bicarbonate solution is comprised within the range of from 0.5 to 3.

5. Coatings according to any of the preceding claims, wherein the binding agent comprises aqueous dispersion of synthetic polymers and/or copolymers.

6. Coatings according to claim 5, wherein the binding agent comprises ethylene-vinyl acetate copolymers in dispersion of polyurethanes in dispersion, with concentrations of the latexes comprised within the range of from 20 to 50% by weight.

7. Coatings according to any of preceding claims, wherein the binding agents comprise co-binding agents.

8. Coatings according to claim 7, wherein the co-binding agents comprise anionic type products such as the salified polymer of acrylic and/or methacrylic acid in the form of ammonium salts.

9. Coatings according to any of the preceding claims, wherein kaolinites, attapulgites or clay materials with a granulometry equal to or lower than 100 micrometers are added to the paste.

10. Flexible coatings for the sulphation-removing cleaning of frescoed surfaces, comprising a fibrous support impregnated with a binding agent and with a paste of an anion-exchange material in powder form in water.

11. Coatings according to any of the preceding claims, wherein said coatings, after the impregnation, are dried and exsiccated at a mild temperature not higher than 50° C.

12. Coatings according to any of the preceding claims, wherein said coatings, at their use time, are reconditioned in demineralized water or in suitable solutions of ammonium carbonate and/or bicarbonate.

13. Use of the coatings according to any of the claims 1 to 12 in the quantitative determination of the sulphation degree, in the sulphation removal, in the cleaning from the materials of proteinic nature, or frescoed surfaces of plasters of prevailingly carbonatic nature.

14. Process for the preparation of flexible coatings according to any of the claims 1 to 12 comprising the impregnation of a fibrous support with a binding agent and with a paste comprising an aqueous solution of ammonium carbonate and/or bicarbonate and/or an anion exchange material in powder form.