

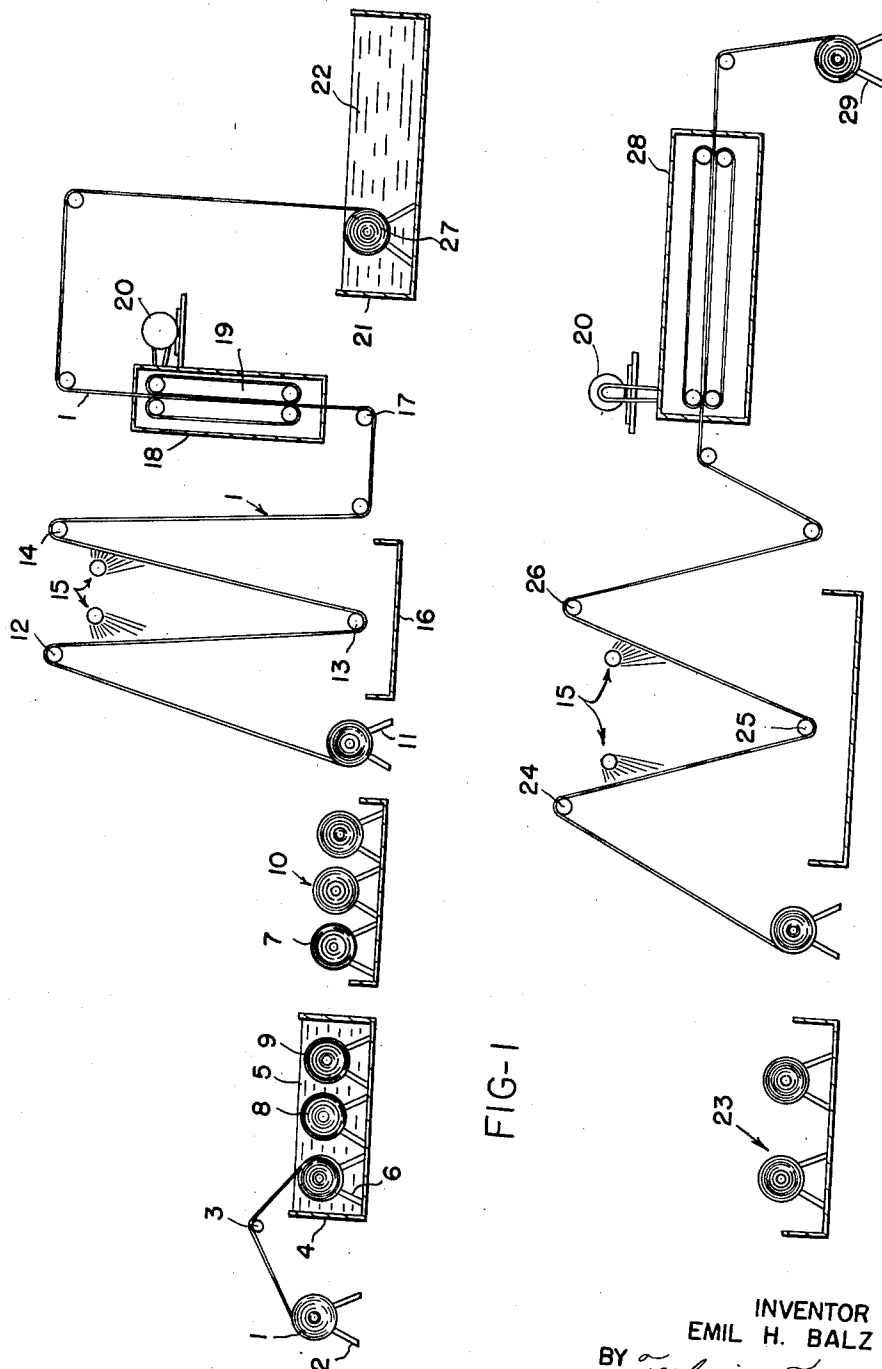
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E. H. BALZ
METHOD OF CLEANING GLASS CLOTH

2,674,549

Filed May 28, 1951

3 Sheets-Sheet 1



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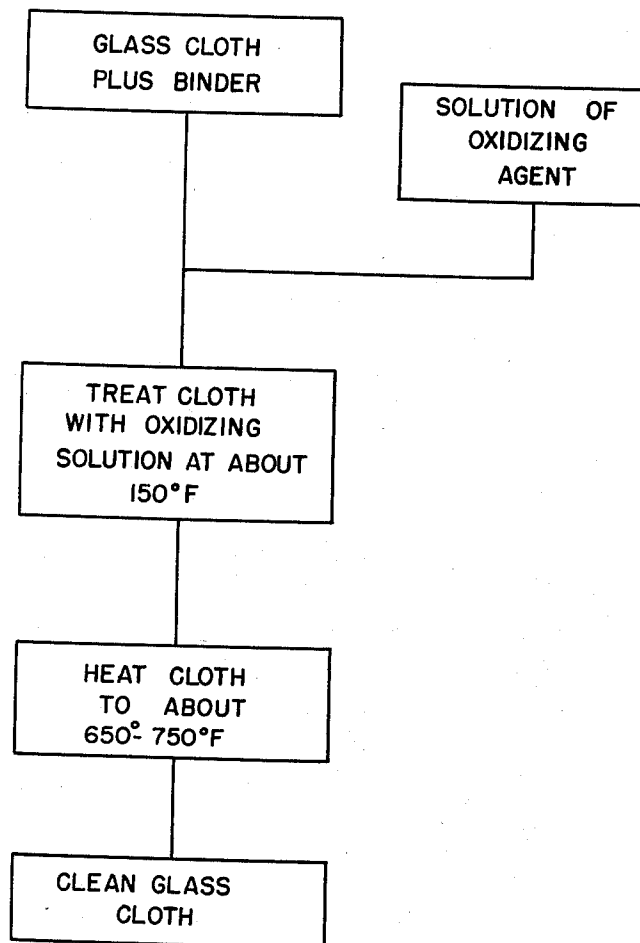
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3 Sheets-Sheet 2

FIG-2



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3 Sheets-Sheet 3

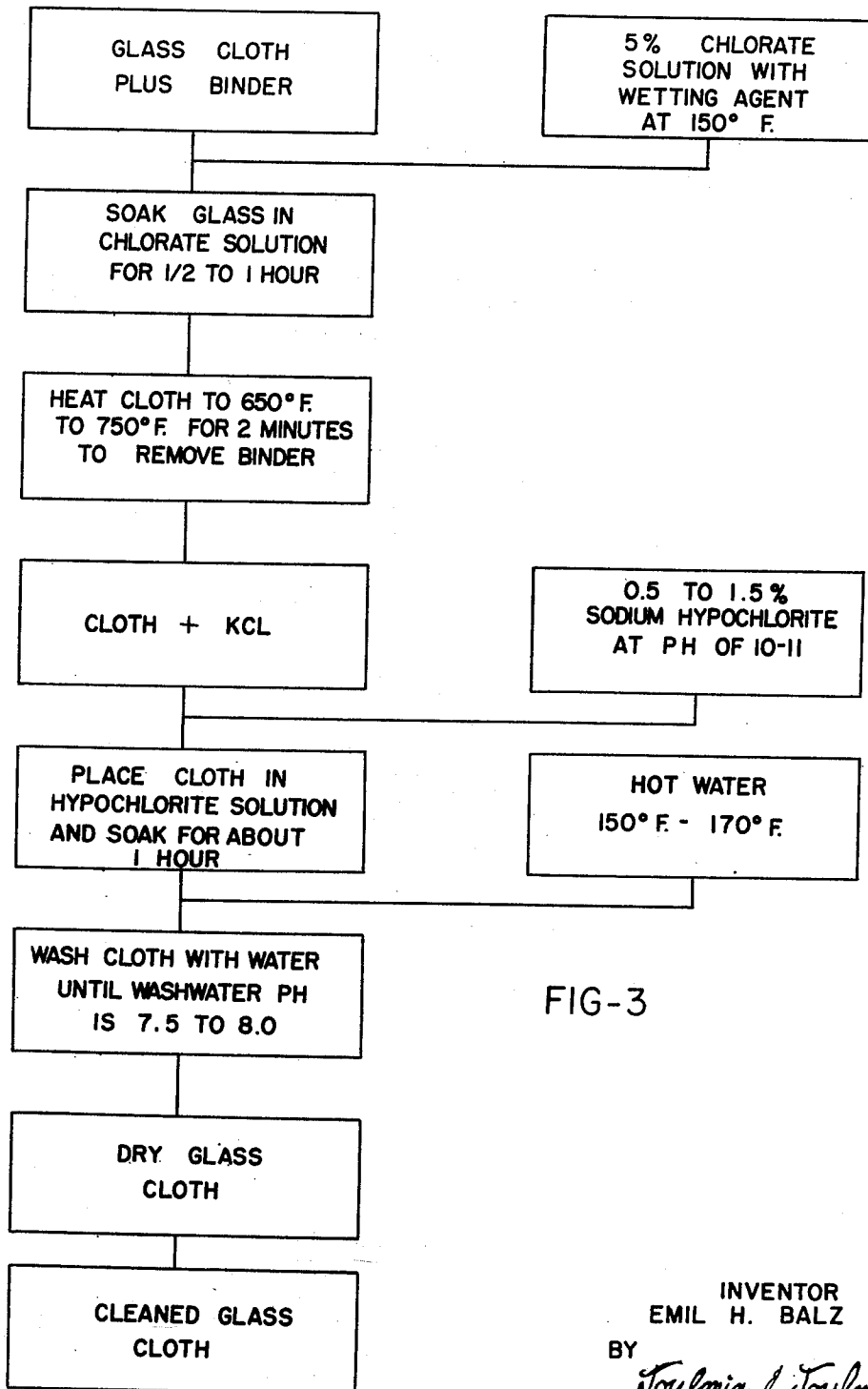


FIG-3

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METHOD OF CLEANING GLASS CLOTH

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Application May 28, 1951, Serial No. 228,624

14 Claims. (Cl. 134—2)

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This invention relates to glass cloth. More particularly the invention relates to a treatment for glass cloth to render the same useful in the making of laminations with resinous materials.

In the production of glass cloth the glass composition is first made molten and caused to flow from extremely small orifices from which it is picked up by a revolving drum or an air or high pressure steam blast and pulled into long fine fibers. The individual fiber is smooth, substantially cylindrical and normally has a diameter of about .00021 to .00040 inch. The fibers may then be grouped in such fashion as to form a thread of parallel fibers and thereafter a group of the continuous fibers is sent on to the textile machines for weaving into cloth.

In order to minimize friction in processing, the fibers while they are being drawn out are treated with a water dispersion of a lubricant or binder material prior to formation of the groups. This binder material, which generally consists of a vegetable lubricating oil, starch and very small amounts of wetting and dispersing agents, etc., coats the fibers and remains thereon in the finished glass cloth. The binder is present to the extent of about 1.5% to 2.0% by weight on the dry finished glass cloth.

The presence of this binder aids in the textile operation but seriously affects the ability of the glass cloth to form laminates with other materials, such as synthetic resins. Accordingly, when it is desired to form such laminates treatment of the glass cloth to remove the binder material is required in order to obtain satisfactory adhesions between the cloth and the resin.

Present known methods for the removal of the binder require among other steps the treatment of the cloth at temperatures of the order of 600 to 700° F. for prolonged periods, generally 55 to 60 hours. Such methods, of course, seriously hinder production, require an excessive amount of equipment for a given production, and in the overall are exceedingly expensive.

The present invention contemplates the provision of a novel method for the removal of the binder material from the glass cloth utilizing a short moderate heat cycle.

The invention further contemplates a method of providing a scrupulously clean glass cloth surface particularly suitable for combining with resinous compositions.

The invention also contemplates the provision of a production method for the cleaning of the glass cloth which eliminates the necessity for

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large storage space requirements during the processing steps.

I have found that these and other objects of the invention may be attained by treating the glass cloth containing the oil-starch binder material with a strong oxidizing agent and thereafter heating the cloth for a matter of about ½ minute or slightly longer at moderate temperatures. The treated binder is reacted by this treatment and in effect is burned from the glass cloth.

In the practice of the invention the glass cloth is first treated with a strong chlorate solution, that is about 3 to 10% by weight of chlorate, at a temperature of about 150° F. Detergents or wetting agents are employed in the chlorate solution to assist in the penetration and wetting of the cloth.

The wet cloth may then be subjected to the action of the heating step to effect removal of the binder. The chlorate, which is of itself stable at temperatures of up to about 900° F. will in the presence of the binder at the heating temperature break down, releasing oxygen, which acts on the binder to decompose it and remove it from the cloth. Any slight discoloration present on the cloth due to decomposed binder may thereafter be eliminated by subjecting the cloth to the action of a bleaching agent, the excess of which may then be removed if necessary by washing with water.

The treatment of the invention is adaptable to all oil-starch binder materials and in substantially all proportions of these components. The oil of the binder is generally a lubricating oil of vegetable origin, such as castor, hydrogenated cottonseed, olive and coconut. Highly unsaturated oils due to their instability to light are not usually employed in the lubrication of fibers for glass cloth manufacture, but if so employed would also be removable from such cloth by the process of the invention. The starch of the binder may be of any of the normal starches of commerce and may include the slightly hydrolyzed or dextrinized materials. In addition to these primary components the binder may contain, in extremely small amounts, one or more substances such as gelatine, borax, polyvinyl alcohol, a cationic agent or other wetting and dispersing compounds.

These ingredients are set forth by way of illustration only since the inventive concept is applicable to the removal of all components which after treatment by the oxidizing agent are in such a condition as to render them readily removable from the cloth by the ignition step de-

scribed in detail hereinafter. In most instances these secondary components may of course be readily selected in the first instance in order that the desired end be achieved.

The oxidizing agents which are particularly suitable for the process of invention include the chlorates of sodium, potassium, calcium, barium, strontium and magnesium. The prime requirements of the oxidizing agent for production purposes are that the agent have strong oxidizing powers, be adaptable to simple production equipment, not deleteriously affect the glass and be soluble at moderate temperatures.

Bleaching of the cloth where necessary may be effected in any suitable medium which does not attack the glass cloth, the prime purpose of this step being to effect complete cleaning of the glass surface by removing any chloride present and any discoloration due to binder residue. Thus exposure of the cloth to an oxidizing atmosphere, such as oxygen gas, may effectively be employed. However, it is generally preferred for production purposes to utilize a bleaching solution, such as sodium hypochlorite in water. Other specific bleaching agents may be used subject to the limitations in their selection that they do not attack the glass and that for production purposes they leave little or no residue that may not be washed out with water. Calcium hypochlorite may, for example, be employed, but is somewhat more difficult to wash from the fabric.

I have found that rather moderate temperatures of 650° F. to 750° F. may be used to burn the binder from the treated glass cloth and that the time of exposure to the heat need only be very short, that is, in the range of about ½ to 1½ minutes. For example, a glass cloth containing a binder material to the extent of about 1.8% on the weight of the cloth, the binder consisting essentially of 16 parts of starch and 2 parts of hydrogenated cottonseed oil and negligible amounts of other decomposable material was completely cleaned leaving no residue, by exposure to an oven temperature of 700° F. for about one minute. At an oven temperature of about 750° F. it was found to be possible to cleanse the same cloth in about ½ minute, only a very slight residue remaining on the cloth after ignition, this residue being readily removed by supplemental treatment with a bleaching agent such as hypochlorite. The treatment of invention therefore permits of a very short operating cycle to be described more fully in the specific example detailed hereinafter.

Detergent and wetting agents particularly useful in the oxidizing solution are those such as Triton N-100 which is a concentrated wetting agent and detergent designed primarily for use in the textile trade. Such an agent assists in the wetting and penetration of the cloth binder which of itself is somewhat water repellent due to the oil content thereof. Triton N-100 is a concentrated wetting agent and an aryl alkyl polyether alcohol soluble in all proportions in cold water and soluble in most organic compounds.

The surface of the glass cloth thus cleaned acquires a hydroxyl group since the glass is hydrolyzed by the action of the alkaline bleaching agent. The presence of this anion assists adhesion between the glass and the resin layer to be applied thereto, and is of a particular benefit where a cationic agent such as methacrylate chromic chloride (Volan) is applied to the glass to form thereon an adsorbed film containing reactive double bonds which combine readily with

organic materials such as the polyesters. The formation of these laminates is of itself known to the art and forms no part of the present invention. However, the subject matter contained in my copending application, Serial No. 235,161, filed July 5, 1951, is directed to an improvement of the known process of laminate formation. This application is also related to Serial No. 228,623, filed May 28, 1951.

The invention will be more fully understood by reference to the following detailed description and appended drawings wherein:

Figure 1 is a diagrammatic representation of apparatus used in the preferred embodiment of the invention.

Figure 2 is a flow sheet illustrating the process of invention; and

Figure 3 is a flow sheet illustrating a further embodiment of the process of invention.

Referring to Figure 1, there is shown a roll of glass cloth 1 produced from standard "E" glass, the fibers of which during manufacture were treated with an aqueous binder material consisting by weight of about 2% of hydrogenated cottonseed oil (Pureco), about 8% of partially dextrinized starch (Globe gum), about .06% of gelatin, about .13% of polyvinyl alcohol, about .2% of Tween 81 (partial esters of fatty acids and hexitolanhydrides combined with polyoxyethylene chains), about .4% of onyx cation X (fatty imidazoline derivative), the balance being water and a very small amount of borax to bring the pH of the dispersion into the range of 6.0 to 6.6. This binder material, minus the water content, is present to the extent of about 1.8% by weight on the dry glass cloth roll shown at 1.

The roll of glass cloth 1 is shown mounted upon a stand 2 and may be appropriately unreel and passed over an idler roller 3, into a tank 4 containing an aqueous solution of potassium chlorate having a chlorate concentration of about 5%, approximately .05 to 0.1 of 1% by weight of the solution of Triton N-100 wetting agent and an aryl alkyl polyether alcohol soluble in all proportions in cold water, as detergent, indicated generally at 5. This treatment serves to remove a portion of the starch and soluble borax and gelatin from the cloth and to render the binder remaining susceptible to the temperature treatment described hereinafter. The cloth is rerolled in the solution on stand 6 and permitted to soak for about ½ to 1 hour, whereupon it is removed from the chlorate solution and stored as at 7 to await further processing. It is clear that a number of rolls may be subjected to the action of the chlorate at one time as indicated at 8, 9 and that a small storage space indicated generally at 10 will accommodate a considerable number of treated rolls.

The cloth, preferably while still wet with the oxidizing solution, may be unreel from a stand 11 and passed directly to oven 12. Alternatively the cloth prior to entering the oven may be further wet with oxidizing solution by passing the fabric continuously over rolls 12, 13 and 14 and under sprays indicated generally at 15. These sprays, if utilized, are supplied with oxidizing solution 5 in which case a pump (not shown) is provided to move the liquid from tank 4 to these sprays. Solution 5 will contain dispersed starch as well as the primary ingredients of the solution, and the presence of the dispersed starch enhances the spray action. Where the spray of oxidizing solution is employed the spent spray liquid may be recirculated to tank 4.

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The cloth, treated with the oxidizing agent either by soaking alone, or by soaking plus the spray treatment noted, is then passed under a spreader roller 17 and thence to oven 18, which operates at a temperature of approximately 650° F. to 750° F. and wherein a conveyor indicated at 19 driven through power means denoted at 20 supplies motive power to the cloth. The oven has an overall length of about 12 feet and the conveyor may be operated at controlled adjustable speeds of between about 2 to 30 feet per minute, and in the instance under consideration the cloth and conveyor were driven at about 12 feet per minute, the cloth assuming in the latter part of the oven to traverse a temperature of about 600° F. to 650° F. It may be noted that generally it is desirable to induce movement of the cloth by providing motive means on one or more of the rolls over which the cloth passes, as will be understood by one skilled in the art.

The chlorate treated binder, including the polyvinyl alcohol, cation X and dispersing agents present, it has been found, will be driven off completely by the spraying and igniting action under the conditions indicated above, which as may be readily derived from the foregoing, involves the application of heat to the cloth for only about one minute.

In a further embodiment of the invention the chlorate treated cloth was passed to the oven operating at a temperature of about 700° F. and an oven conveyor speed of about 20 to 24 feet per minute and only a trace of binder remained on the cloth after the heat treatment. Under this condition the heated glass cloth may be passed continuously into a tank 21 containing a 0.5% aqueous solution of hypochlorite having a temperature of about 75° to 85° F.

Preferably the cloth is wound on reel 27 in the solution indicated at 22 and allowed to soak therein for about ½ to 1 hour. Alternatively the cloth may be simply passed through the hypochlorite solution and stored as indicated generally at 23, in which case the storage time should also be approximately 30 minutes.

Upon completion of the bleaching treatment the excess bleaching agent is washed from the cloth with water having a temperature in the range of 150° to 170° F. by passing over rolls 24, 25, 26 and thereafter dried, and a completely cleaned glass cloth is attained in an overall production time for a given roll of less than about 2½ to 3 hours.

The cleaned glass cloth thus produced will laminate readily with silicone resin and when the cleaned cloth is first treated with a cationic agent such as Volan, as discussed briefly hereinbefore, a bond with the polyesters may be effected.

In yet another embodiment of the invention the glass cloth may be treated directly with a spray of a water solution containing approximately 5% chlorate directed onto the cloth by means of the nozzles indicated generally at 15 in Figure 1. In this instance soaking of the rolled cloth in the chlorate solution is not necessary and the action of the spray removes a proportion of the binder material from the cloth, the balance of the binder being removed by the action of heat as noted hereinbefore. In this instance the spray solution for reasons of economy is preferably recirculated in which case the spray will contain a quantity of dispersed starch, which as noted hereinbefore assists in the removal of the binder.

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Accordingly it is clear that by suitable regulation of the heating conditions, cloth containing binder material treated with an oxidizing agent, may be suitably cleaned by a short moderate heat cycle.

While the production time for a given roll of cloth will vary somewhat with particular operating conditions and equipment available, it will be appreciated that the complete treatment time of less than 3 hours is a material improvement over the present practice wherein a matter of several days is required for the complete procedure.

In each of the detailed examples set forth hereinbefore, the chlorates of sodium, magnesium, strontium, barium or calcium may be substituted for the potassium chlorate. The chlorides resulting from the decomposition of these chlorates similarly to potassium chloride have a melting point in excess of the temperature range employed in the invention, and accordingly no possibility of fusion with the glass exists.

All glass compositions suitable for the production of glass fabrics may be employed in the process of invention and the glass will not be affected thereby. Particularly it should be noted that no decrease in strength of the fabric occurs during the treatments set forth.

It is to be understood that other oxidizing agents may be substituted for those specifically set forth hereinbefore, that the time and temperature of heating and selection of bleaching agents are susceptible to modification and that the equipment and other factors may be altered to adapt them to different usages and conditions and, accordingly it is desired to comprehend such modifications within this invention as may fall within the scope of the appended claims.

I claim:

1. In a method of removing oil-starch binder material from glass cloth the steps of impregnating the cloth with an aqueous solution of a heat decomposable chlorate selected from the group consisting of the alkali and alkaline earth metal chlorates which chlorate is capable of liberating oxygen upon heat decomposition, removing the cloth from the solution, and heating the impregnated cloth to a temperature sufficient to decompose the said chlorate and said binder material.

2. In a method of removing oil-starch binder material from glass cloth the steps of impregnating the cloth with an aqueous solution of a heat decomposable chlorate selected from the group consisting of the alkali and alkaline earth metal chlorates which chlorate is capable of liberating oxygen upon heat decomposition, removing the cloth from the solution, heating the impregnated cloth to a temperature sufficient to decompose the said chlorate and said binder material, and bleaching the cloth to remove any residue remaining thereon.

3. In a method of removing oil-starch binder material from glass cloth the steps of impregnating the cloth with an aqueous solution containing by weight about 3 to 10 percent of potassium chlorate, removing the impregnated cloth from the solution, and thereafter heating the cloth to a temperature of about 650-750° F. to decompose the potassium chlorate and the binder material.

4. In a method of removing oil-starch binder material from glass cloth the steps of impregnating the cloth with an aqueous solution containing by weight about 3 to 10 percent of potassium chlorate, removing the impregnated cloth from the solution, thereafter heating the cloth

to a temperature of about 650-750° F. to decompose the potassium chlorate and binder material, and then bleaching the cloth to remove any residue remaining thereon.

5. In a method of removing an oil-starch binder material from glass cloth, the steps of impregnating the cloth with an aqueous solution of potassium chlorate, removing the impregnated cloth from the solution, and thereafter heating the cloth to a temperature of about 600° F. to 650° F. to decompose the potassium chlorate and binder material.

6. In a method of removing oil-starch binder material from glass cloth the steps of impregnating the cloth with an aqueous solution of potassium chlorate, removing the cloth from the solution, and thereafter heating the cloth to a temperature of about 650° F. to 750° F. to decompose the potassium chlorate and binder material, and then bleaching the cloth to remove any residue remaining thereon.

7. A method of cleaning glass cloth from oil-starch binder material comprising the steps of impregnating the cloth with an aqueous solution containing about 3-10 percent by weight of potassium chlorate for about one hour, removing the cloth from the solution, heating the cloth to about 650 to 750 degrees Fahrenheit for about one minute to decompose the potassium chlorate and burn off the binder material, soaking the cloth in an aqueous solution of sodium hypochlorite at a pH of about 10 to 11 for about one hour, and washing the cloth to remove any excess sodium hypochlorite remaining thereon.

8. In a method of removing oil-starch binder material from glass cloth the steps of impregnating the cloth with an aqueous solution containing about 3-10 percent by weight of a metal chlorate selected from the group of sodium, potassium, magnesium, calcium, barium and strontium chlorates, removing the cloth from the solution, thereafter heating the cloth to a temperature of at least that of the decomposition point of the chlorate impregnated in the cloth and below that of the fusion point of the chloride produced by the decomposition of the chlorate thereby liberating oxygen and decomposing the binder material, and then bleaching the cloth to remove any residue remaining thereon.

9. In a method of removing oil-starch binder material from glass cloth the steps of impregnating the cloth with an aqueous solution containing about 3-10 percent by weight of potassium chlorate at a temperature of about 150° F., removing the cloth from the solution, and thereafter heating the impregnated cloth to a tem-

perature of about 650° F. to decompose the potassium chlorate and binder material.

10. In a method of removing oil-starch binder material from glass cloth the steps of impregnating the cloth with an aqueous solution containing about 5 percent by weight of potassium chlorate at a temperature of about 150° F. for about ½ to 1 hour, removing the cloth from the solution, and thereafter heating the impregnated cloth at a temperature of about 700° F. for about one minute to decompose the potassium chlorate and binder material.

11. In a method of removing oil-starch binder material from glass cloth the steps of impregnating the cloth with an aqueous solution containing about 5 percent by weight of potassium chlorate at a temperature of about 150° F. for about ½ to 1 hour, removing the cloth from the solution, heating the impregnated cloth at a temperature of about 750° F. for about one-half minute, and thereafter bleaching the cloth to remove any residue remaining thereon.

12. In a method of removing oil-starch binder material from glass cloth the steps of impregnating the cloth with a spray of a water solution containing about 5% potassium chlorate and thereafter heating the cloth in air at a temperature of about 650° to 750° F. to remove the binder material therefrom.

13. In a method of removing binder material from glass cloth the steps of impregnating the cloth with a spray of a water solution containing about 5% of potassium chlorate and dispersed starch, removing the cloth from the spray, and thereafter heating the cloth in air at a temperature of about 650° F. to 750° F. to remove the binder material therefrom.

14. In a method of removing binder material from glass cloth the steps of soaking the cloth in a water solution containing about 3-10 percent by weight of potassium chlorate at a temperature of about 150° F., removing the cloth from the solution, spraying the cloth with a potassium chlorate solution containing starch, thereafter heating the cloth at a temperature of about 650° F. to 750° F. in air to remove the binder material therefrom, and washing the cloth with water.

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