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PURIFICATION

Earl Thayer Ellis, Petersburg, Va., assignor to
E. I. du Pont de Nemours & Company, Wil-
mington, Del., a corporation of Delaware

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This invention relates to the removal of lead, iron and like metals, free or in a combined state, from aqueous treating media, and more particularly to the purification of dilute aqueous solutions of regenerated cellulose softener baths.

In recent years the use of regenerated cellulose sheet as a wrapping material has become wide-spread. Since the transparency of such material has contributed in a large measure to its acceptance, much time and money has been spent in efforts to improve its clarity. This sheet material (which in its commonest form has a thickness of about 0.001 inch) as at present produced exhibits considerable discoloration when viewed as a tightly wound roll or a stack consisting of a number of sheets.

It has now been discovered that metallic impurities in general (and lead in particular) in the softener bath are chiefly responsible for the poor appearance, since a product having crystal-clear transparency can be obtained when metal-free baths are employed.

In the manufacture of regenerated cellulose pellicles by the viscose process, it is necessary to give a pellicle, in the course of production extensive treatment with aqueous baths. Since many of these baths are corrosive for such well known materials of construction as sheet iron, wood, etc., it has become common practice to line the treatment vats with sheet lead. These linings are free from leaks, stand up well with the solutions used, and are easily repaired. When such tanks are used, traces of lead are deposited (presumably through the medium of the bath) upon the surface or incorporated in the pellicle of cellulose being treated. Although the amount of lead is extremely small, it is sufficient (especially upon action of sulfur in the atmosphere) to produce undesirable and detrimental discoloration in the pellicle.

The provision of means for the removal of very small traces of lead and other detrimental metals or metallic compounds from aqueous solutions, was an object of this invention. It was a further object to provide a means of removing lead and lead compounds from aqueous solutions of glycerol and/or glycol. It was a still further object to provide a continuous method for the purification of aqueous treating baths containing glycerol and/or glycol and like softeners. The avoidance of discoloration in softened regenerated cellulose sheet produced from viscose, and the removal of lead and like metals both free and in combination from glycerol

softener baths for regenerated cellulose, constitute still other objects of this invention. A general advance in the art, and other objects which will appear hereinafter, are also contemplated.

In general the objects of this invention are attained by circulating an aqueous treating bath, such as, for example, one containing glycerol and/or glycol, through a bed of diatomaceous earth. It has been impossible to remove these materials by well known adsorptive agents such as activated carbon, and it is most surprising that a material such as diatomaceous earth should have this selective adsorption for lead and lead compounds (as well as other metallic impurities). For convenience, this invention will be described in terms of the manufacture of regenerated cellulose pellicles by the viscose process. Viscose, after extrusion from a suitably shaped orifice and subsequent treatment as described in United States Patent No. 1,548,864, is (before drying) passed through a glycerol and/or glycol solution, which impregnates it with a suitable amount of glycerol and/or glycol to serve as a softener in the finished product. The softener bath is continuously filtered through diatomaceous earth. A durable, highly transparent and flexibilized structure of desirable clarity, containing a small percentage of water in addition to the glycerol and/or glycol, results.

The treating bath for the impregnation with glycerol and/or glycol is kept in proper condition by circulating through appropriate apparatus, to which may be added additional material, as well as mold inhibitive substances. Pasteurization of the bath for the inhibition of mold growth, and heating facilities for maintaining the bath at the desired temperature, may also be employed.

From the following description and specific examples, in which are disclosed certain embodiments of the invention as well as details of what is believed to be the best mode for carrying out the invention, it will be apparent how the foregoing objects and related ends are accomplished. The quantities are given in parts by weight throughout the application, unless otherwise indicated.

Example I

A 5% aqueous solution of a mixture of glycerol (6 parts) and glycol (4 parts) which had been used in the manufacture of regenerated cellulose sheeting, and which gave an undesirably discolored finished product, was filtered by gravity through a one-fourth inch layer of diatomaceous earth. Before filtration, the solu-

tion was slightly yellow and turbid, turbidity being 45 by the American Public Health Association standard. After filtration, the solution was water white and sparkling clear with a turbidity of 1.4 by the above standard. The unfiltered bath contained colored metal and/or metal-compounds, including 4.0 p. p. m. of lead and 0.4 p. p. m. of iron. Filtration reduced these to 0.7 p. p. m. lead and 0.04 p. p. m. iron. When reused, the finished regenerated cellulose film had satisfactory clarity. The diatomaceous earth sold under the trade name "Super-Cel" works excellently in this procedure and gives an equal reduction in lead and iron content. This material is a calcined diatomaceous earth which gives a filtration flow about twice as great as untreated diatomaceous earth.

Filtration of this and similar aqueous glycerol or ethylene glycol solutions through the finest filter paper, pads of pulp (paper) or cotton fiber, powdered carbon and the like, will under very favorable conditions reduce turbidity and the metal content only to about one-half the amount set out above as being present originally. The resultant solutions do not permit the production for finished sheet of satisfactory clarity.

Example II

A 5% aqueous glycerol—ethylene glycol solution was filtered through a one-eighth inch layer of diatomaceous earth having a total filter area of 900 square inches. The filtered solution was supplied directly to tanks in which transparent regenerated cellulose sheeting was treated, and then returned for refiltration. The rate of cycling of the solution was 50 gallons per minute. The filtration process maintained bath turbidity, lead and iron concentrations at 2.4, 0.47 p. p. m., and 0.07 p. p. m., respectively. The appearance of the finished sheeting as greatly improved after the filtration of the bath had taken place.

Similar treatment, but with the softening solution filtered through a fine grade of cotton flannel, resulted in no better than a somewhat milky yellowish bath having bath turbidity, lead and iron concentration of 60, 10.8 p. p. m., and 0.70 p. p. m., respectively. The final sheeting was undesirably discolored.

The diatomaceous earth sold under the trade name "Hyflo Super-Cel" is especially suitable for this procedure. This material is a calcined and chemically refined diatomaceous earth having about four times the flow of untreated diatomaceous earth.

Various grades of diatomaceous earth are satisfactory for filtering the softener baths for the removal of lead and other metallic impurities. Removal of 95% or more of the metals and metal compounds is possible using the diatomaceous earth sold under the trade name "Celite." This industrial grade comprises the refined diatom skeleton material from the California deposits, and has a graded fineness of approximately 10 microns in size.

This method of purification may be applied to softener baths of various descriptions. In addition, it may be found advantageous to apply the treatment to other tanks in the casting machine, such as the wash water tanks, bleaching solution, coagulation and regeneration baths.

The process is particularly useful where the vats themselves are lined with lead, but may also be found advantageous for the linings of iron, or where lead or iron piping is used in the

circulating system or conditioning apparatus of the bath employed.

The diatomaceous earth may be added to the bath material before it enters the filter, and the filtering pad built up gradually.

The filtration process described above can be used advantageously for the removal of lead, iron and the like from aqueous treating media, particularly dilute aqueous glycerol and/or glycol solutions in general. It follows that the procedure described is applicable to other arts than the production of transparent sheets from aqueous alkaline cellulosic solutions coagulable in acid coagulating baths.

By the procedures of this invention, an extremely pure and highly transparent pellicle of regenerated cellulose may be obtained because of the removal of impurities such as lead and lead compounds.

Numerous treatment baths may be given the purification of this invention in order to remove the metallic impurities which, in very small traces, will be detrimental, either from the point of view of the appearance of the resulting product or toxicity of such a product.

No other method has been discovered for removing extremely small quantities with absolute efficacy which at the same time is so simple and so reliable. Furthermore, this process does not depend upon chemical treatment, which, in general, introduces other materials which may be undesirable or detrimental to the product.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. The process of removing materials causing discoloration of regenerated cellulose sheet from softener baths for regenerated cellulose webs which comprises filtering the contaminated softener bath through diatomaceous earth.

2. The process of removing materials causing discoloration of regenerated cellulose sheet from glycerol softener baths for regenerated cellulose webs which comprises filtering the contaminated glycerol bath through diatomaceous earth.

3. The process of removing materials causing discoloration of regenerated cellulose sheet from glycol softener baths for regenerated cellulose webs which comprises filtering the contaminated glycol bath through diatomaceous earth.

4. The process which comprises passing an aqueous 5% glycerol solution, which has been used as a softening bath in the manufacture of regenerated cellulose sheeting until it causes the finished product to be undesirably discolored, through a bed of diatomaceous earth at least $\frac{1}{4}$ " thick.

5. The process which comprises passing an aqueous regenerated cellulose sheet softener solution, which has been used as a softening bath in the manufacture of regenerated cellulose sheeting until it causes the finished product to be undesirably discolored, through a bed of diatomaceous earth at least $\frac{1}{8}$ " thick.

6. The process of claim 4 when the diatomaceous earth is a calcined type.

7. The process of claim 5 when the diatomaceous earth is a calcined type.

8. The process of removing materials causing discoloration of regenerated cellulose sheet from softener baths for regenerated cellulose webs

which comprises filtering the contaminated bath through diatomaceous earth, the said softener bath containing, as softener, material from the group consisting of glycerol and glycol.

9. The process of removing metal materials 5 causing discoloration of regenerated cellulose sheet from softener baths for regenerated cellulose webs which comprises filtering the contaminated softener bath through diatomaceous earth.

10. The process of removing lead materials 10

causing discoloration of regenerated cellulose sheet from softener baths for regenerated cellulose webs which comprises filtering the contaminated softener bath through diatomaceous earth.

11. The process of removing iron materials causing discoloration of regenerated cellulose sheet from softener baths for regenerated cellulose webs which comprises filtering the contaminated softener bath through diatomaceous earth.

EARL THAYER ELLIS.