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ARTIFICIAL MATERIAL AND PROCESS FOR MAKING SAME.

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In my co-pending application No. 113,582, filed June 3, 1926, for "artificial material and process for making same," a process is described, wherein sulphuric acid containing at least 55 per cent of H_2SO_4 , preferably sulphuric acid containing 65 to 85 per cent of H_2SO_4 is used as coagulating bath for viscose.

The present invention is based upon the discovery that viscoses containing not more than 5 per cent of caustic alkali (calculated as NaOH), when brought into the form of an artificial material such as threads, films, bands or plates, yield lustrous products when coagulated with sulphuric acid containing not less than 45, but less than 55 per cent of H_2SO_4 .

Any viscose prepared according to any process or method known hitherto from an alkali cellulose that has been matured as usual in the artificial silk art, for example for 72 hours, or that has not been matured at all or that has been matured for a shorter time than such as is usual in the artificial silk art, for example for 3 to 48 hours, may be used in the present process, provided that the viscose does not contain more than 5 per cent of caustic alkali (calculated as NaOH).

This aim can be attained for example by dissolving the sulphidized mass either in water or in a caustic soda solution weak enough not to allow the total content of the final viscose in caustic soda to exceed 5 per cent calculated on the weight of the final viscose solution.

Such viscose is brought into the form of an artificial material and coagulated by means of strong sulphuric acid, for example sulphuric acid containing 45 to 55 per cent of monohydrate. In most cases, for instance in manufacturing artificial threads or filaments, or films, or bands, or plates, this can be effected in such a manner that the viscose is caused to pass through suitably formed openings into strong sulphuric acid, for instance acid of 45 to 55 per cent strength (calculated on H_2SO_4) or into a bath containing 45 to 55 per cent of monohydrate. The sulphuric acid may be employed by itself or in admixture with one or more suitable inorganic substances, for example with another strong mineral acid such as hydrochloric acid, nitric acid or phosphoric acid, or with a neutral or acid

salt, such as sodium sulphate, sodium bisulphate, ammonium sulphate, zinc sulphate, sodium bisulphite, sodium sulphite, sodium nitrite, boric acid or the like. To the strong sulphuric acid or its mixture with another strong acid or with one or more of the inorganic substances mentioned above, there may be added one or more organic bodies, such as glycerol or a sugar, for example glucose, or alcohol or a salt of an organic base, for example of aniline, or an organic acid, such as acetic acid or formic acid or lactic acid or oxalic acid. If a salt is added which is capable of reacting with the strong sulphuric acid under formation of an acid sulphate, or which mutually interacts with the sulphuric acid, the strength of the sulphuric acid should be so chosen that, after the amount required for the formation of the acid sulphate or for the mutual interaction is used up, the coagulating bath contains free sulphuric acid of the desired strength, but at any rate not less than 45 parts by weight of monohydrate in 100 parts by weight of the precipitating bath.

If desired, there may be added to the viscose one or more suitable substances known in the viscose-silk art, for example glycerol or glucose or sodium sulphate or sodium sulphite or sodium bisulphite or ammonium sulphate or an alkali silicate or an alkali aluminate or ammonia.

The precipitating bath may be kept at room temperature or at a temperature exceeding room temperature, for example at 25 to 40° C., or at a temperature lower than room temperature, for example at 0 to 5° C., or even below 0° C., for example at from -1 to -10° C.

The length of immersion of the thread or filament or plate or film or band in the strong sulphuric acid or in the bath containing it may be varied within wide limits, for example from 3 to 60 centimetres and even more, for instance 1 to 2 meters.

If desired the thread or film or band may be stretched either immediately after its formation, i. e. in the precipitating bath containing, or consisting of, sulphuric acid, of 45 to 55 per cent strength or subsequently, i. e. after it has been removed from the bath, i. e. between the precipitating bath and the collecting device, for instance bobbin or centrifuge.

The thread or film or band or plate or

coated or impregnated material may, after washing, be heated or steamed before or after drying.

The process being open to manifold variations, it is not intended to confine the invention to the following examples given for the practical carrying out of the process.

I (a) to (c)

(a). 100 parts by weight of sulphite-pulp or linters are impregnated with 900 to 2000 parts by weight of a caustic soda solution of 18 per cent strength at 15 to 18° C., and the mixture allowed to stand for 3 to 24 hours. Then the mass is pressed to 300 parts by weight, and the residue comminuted by hand or in a suitable apparatus, for instance in a cooled shredder. The comminuted soda cellulose is then kept at room temperature for 60 to 72 hours, whereupon 30 to 60 parts by weight of carbon bisulphide are added, and the reacting mixture, preferably under stirring (for example in a closed kneading machine) or agitating (for example in a sulphidizing drum), kept for several (for example 4 to 12) hours at 16 to 20° C. Thereafter the excess of the carbon bisulphide is removed by driving off or evacuating, and the sulphidized mass, the weight of which is 348 parts by weight is dissolved in 600-700 parts by weight of water or in 400-500 parts by weight of a caustic soda solution of 1 to 1.3 per cent strength. The viscose solution thus obtained is then filtered in a known manner through cotton wool or a dense cotton fabric or through both and freed from gas bubbles if any. Immediately after, or after it has been allowed to ripen at 16-18° C. for a shorter (for example 12 hours to two days) or a longer (for example three to four days) time, the viscose is spun in a known manner into one of the following precipitating baths:

- (1) Sulphuric acid of 60° Bé., or
- (2) Sulphuric acid of 55° Bé., or
- (3) A solution of 13.3 parts by weight of ammonium sulphate in 120 parts by weight of sulphuric acid of 55° Bé., to which 9 to 10 parts of sulphuric acid of 66° Bé. have been added, or
- (4) A solution of 10 to 15 parts by weight of glucose in 190 to 185 parts by weight of sulphuric acid of 55° Bé.

The temperature of the precipitating bath is kept at 0 to 16° C., for instance at 8° C., or at -4 to -8° C.

The length of immersion in the coagulating bath of the threads forming therein may be short for example 10 centimetres or long for instance from 30 to 100 centimetres and more. They are then collected in a known manner on a bobbin or in a spinning centrifuge which may be placed either close by the precipitating bath or at a distance from

20 to 120 centimetres from the bath, whereupon the threads are washed and dried.

The threads may be stretched in any known manner whilst they are in the precipitating bath, or after they have been removed from the bath. This may be done for example either by choosing a more or less long distance between the bath and the collecting device, or by leading the threads over rods or hooks arranged in the bath or between the bath and the collecting device, or in the bath and between the bath and the collecting device.

The speed of spinning may be varied within wide limits. As a rule to which, however, the invention is not intended to be confined, it may be assumed that the upper limit of speed possible is dependent partly upon the temperature of the coagulating bath, partly upon the length of immersion, partly upon the distance between the coagulating bath and the collecting device, partly upon the degree of stretching given the thread during spinning, and partly upon the quantity of viscose delivered by the pump. The following examples to which, however, the process is not intended to be limited, may be adduced for the purpose of illustration:

(1) If the coagulating bath is used at a temperature below 0° C., for example at minus 5° C., and if the length of immersion is 60 to 120, for example 80 centimetres, and if the distance between the coagulating bath and the collecting device, for example bobbin, is 60 to 150 centimetres, for instance 120 centimetres, and if the stretching given the thread between the coagulating bath and the collecting device is comparatively high, and if the pump delivers about 2 to 3 cubic centimetres of viscose a minute, then excellent results are obtained with a speed of 18 to 26 meters a minute, or 30 meters a minute, but also a higher speed, for example of 30 to 40 meters a minute may be employed if desired.

(2) If all spinning conditions remain the same as in (1), except that the pump delivers 4 to 5 cubic centimetres of viscose a minute, then, if desired a speed up to 40 to 60 meters a minute may be employed.

(3) If the spinning conditions are exactly as in (1), except that the temperature of the coagulating bath is plus 4 to plus 25° C., for example 8° C., if desired the speed may be up to 50 to 60 meters.

If in (1) the length of immersion or the distance between the coagulating bath and the collecting device or both are shortened, the speed may be increased.

Before being washed, the threads may be treated in any known manner with a precipitating bath known in the viscose-silk art, for example a solution of sodium bisulphate

or sodium bisulphite or with dilute sulphuric acid or the like.

The washed threads may, before or after drying, be heated (for example at 100–110° C.) or steamed.

They may also be treated with any desulphurating or bleaching agent known in the viscose art.

(b). The mode of operation is as in (a), except that 75 to 150 parts by weight of carbon bisulphide are employed for the sulphidizing of the soda-cellulose.

(c). The mode of operation is as in (a) or (b), with the difference that the soda-cellulose is pressed to 200 parts by weight.

II (a) to (c).

Mode of operation as in Example I (a) to I (c), with the exception that the soda cellulose is not allowed to mature at all or allowed to mature for 1 to 48 hours, for example for 3 to 24 hours only.

According to the foregoing examples, it is possible to obtain artificial silk or staple fibre which has a considerably higher dry and wet tenacity than silk spun under same spinning conditions, but by means of chemicals customary in the viscose silk-art, for example by using a known precipitating bath. For example: it is not difficult to produce artificial silk having a dry tenacity of more than 2 grammes per denier, even more than 2,5 grammes per denier, for example 2,8 grammes to 3 grammes and more per denier and a wet tenacity of 1,5 to 2 grammes per denier and more.

III.

A viscose prepared as described in Example I or II is caused to pass through a suitable hopper or slit in one of the coagulating liquors mentioned in Example I, and after having left the precipitating bath, is washed and dried in any known manner.

IV.

A cotton fabric is impregnated or filled or coated once or several times with a viscose prepared according to one of the methods described in Example I or II, for which purpose any suitable machine, such as a padding machine or a back filling machine or a spreading machine may be employed. To the viscose there may be added a filling substance, for instance talcum or china clay or a colouring matter or a pigment such as mica, or soot or a mineral colour or the like. The impregnated or coated material is, without being dried, optionally in the stretched state, taken through one of the precipitating baths described in Example I, whereupon the material is washed and dried.

In the foregoing examples, in the preparation of viscose, instead of wood pulp, there may be used bleached cotton, or cellulose

treated in the cold or in the heat with dilute acids, for example hydrochloric or sulphuric acid, in short any kind of cellulosic bodies employed in, or proposed for the manufacture of viscose.

The expression "artificial material" in the description and claims is intended to mean: artificial threads and filaments of any kind, for example artificial silk, staple fibre, artificial cotton, artificial wool, artificial hair, films, plates, coatings and fillings of any kind.

The expression "heating" in the claims is intended to cover any known kind of heating, steaming included.

The statements in the description and claims regarding percentages relate to percentages by weight.

I claim:

1. Process for manufacturing artificial materials from viscose, which comprises bringing a viscose containing not more than 5 per cent of caustic alkali (calculated as NaOH), into the form of an artificial material and acting upon it with sulphuric acid, containing not less than 45 but less than 55 per cent of sulphuric acid monohydrate.

2. Process for manufacturing artificial materials from viscose, which comprises bringing a viscose containing not more than 5 per cent of caustic alkali (calculated as NaOH), into the form of an artificial material and acting upon it with a coagulating bath, containing not less than 45 but less than 55 per cent of sulphuric acid monohydrate.

3. Process for manufacturing artificial materials from viscose, which comprises causing a viscose containing not more than 5 per cent of caustic alkali (calculated as NaOH), to pass through suitably formed openings into sulphuric acid, containing not less than 45 but less than 55 per cent of sulphuric acid monohydrate.

4. Process for manufacturing artificial materials from viscose, which comprises causing a viscose, containing not more than 5 per cent of caustic alkali (calculated as NaOH), to pass through suitably formed openings into a coagulating bath, containing not less than 45 but less than 55 per cent of sulphuric acid monohydrate.

5. Process for manufacturing artificial materials from viscose, which comprises causing a viscose containing not more than 5 per cent of caustic alkali (calculated as NaOH), to pass through suitably formed openings into a coagulating bath which contains not less than 45 but less than 55 per cent of sulphuric acid monohydrate and at least one other inorganic substance.

6. Process for manufacturing artificial materials from viscose, which comprises causing a viscose containing not more than

5 per cent of caustic alkali (calculated as NaOH) to pass through a coagulating bath containing not less than 45 but less than 55 per cent of sulphuric acid monohydrate and giving the coagulated viscose a length of immersion in the coagulating bath of 30 to 200 centimeters.

7. Process for manufacturing artificial materials from viscose, which comprises causing a viscose containing not more than 5 per cent of caustic alkali (calculated as NaOH) to pass through suitably formed openings into a coagulating bath containing not less than 45 but less than 55 per cent of sulphuric acid monohydrate and stretching the coagulated material in the coagulating bath.

8. Process for manufacturing artificial materials from viscose, which comprises causing a viscose containing not more than 5 per cent of caustic alkali (calculated as NaOH) to pass through suitably formed openings into a coagulating bath containing not less than 45 but less than 55 per cent of sulphuric acid monohydrate and stretching the coagulated material between the coagulating bath and the collecting device.

9. Process for manufacturing artificial materials from viscose, which comprises causing a viscose containing not more than 5 per cent of caustic alkali (calculated as NaOH) to pass through suitably formed openings into a coagulating bath containing not less than 45 but less than 55 per cent of sulphuric acid monohydrate and stretching the coagulated material in the coagulating bath and between the coagulating bath and the collecting device.

10. Process for manufacturing artificial materials from viscose, which comprises causing a viscose containing not more than 5 per cent of caustic alkali (calculated as NaOH) to pass through suitably formed openings into a coagulating bath containing not less than 45 but less than 55 per cent of sulphuric acid monohydrate and heating the artificial material after washing and drying it.

11. Process for manufacturing artificial materials from viscose, which comprises bringing a viscose, prepared from an alkali cellulose which has been allowed to mature from naught to 48 hours, which viscose contains not more than 5 per cent of caustic alkali (calculated as NaOH), into the form of an artificial material and acting upon it with sulphuric acid, containing not less than 45 but less than 55 per cent of sulphuric acid monohydrate.

12. Process for manufacturing artificial materials from viscose, which comprises bringing a viscose, prepared from an alkali cellulose which has been allowed to mature from naught to 48 hours, which viscose contains not more than 5 per cent of caustic

alkali (calculated as NaOH), into the form of an artificial material and acting upon it with a coagulating bath, containing not less than 45 but less than 55 per cent of sulphuric acid monohydrate.

13. Process for manufacturing artificial materials from viscose, which comprises causing a viscose, prepared from an alkali cellulose which has been allowed to mature from naught to 48 hours, which viscose contains not more than 5 per cent of caustic alkali (calculated as NaOH), to pass through suitably formed openings into sulphuric acid containing not less than 45 but less than 55 per cent of sulphuric acid monohydrate.

14. Process for manufacturing artificial materials from viscose, which comprises causing a viscose, prepared from an alkali cellulose which has been allowed to mature from naught to 48 hours, which viscose contains not more than 5 per cent of caustic alkali (calculated as NaOH), to pass through suitably formed openings into a coagulating bath containing not less than 45 but less than 55 per cent of sulphuric acid monohydrate.

15. Process for manufacturing artificial materials from viscose, which comprises causing a viscose, prepared from an alkali cellulose which has been allowed to mature from naught to 48 hours, which viscose contains not more than 5 per cent of caustic alkali (calculated as NaOH), to pass through suitably formed openings into a coagulating bath which contains not less than 45 but less than 55 per cent of sulphuric acid monohydrate and at least one other inorganic substance.

16. Process for manufacturing artificial materials from viscose, which comprises causing a viscose, prepared from an alkali cellulose which has been allowed to mature from naught to 48 hours, which viscose contains not more than 5 per cent of caustic alkali (calculated as NaOH), to pass through suitably formed openings into a coagulating bath containing not less than 45 but less than 55 per cent of sulphuric acid monohydrate and giving the coagulated viscose a length of immersion in the coagulating bath of 30 to 200 centimetres.

17. Process for manufacturing artificial materials from viscose, which comprises causing a viscose, prepared from an alkali cellulose which has been allowed to mature from naught to 48 hours, which viscose contains not more than 5 per cent of caustic alkali (calculated as NaOH), to pass through suitably formed openings into a coagulating bath containing not less than 45 but less than 55 per cent of sulphuric acid monohydrate and stretching the coagulated material in the coagulating bath.

18. Process for manufacturing artificial

materials from viscose, which comprises causing a viscose, prepared from an alkali cellulose which has been allowed to mature from naught to 48 hours, which viscose contains not more than 5 per cent of caustic alkali (calculated as NaOH), to pass through suitably formed openings into a coagulating bath containing not less than 45 but less than 55 per cent of sulphuric acid monohydrate and stretching the coagulated material between the coagulating bath and the collecting device.

19. Process for manufacturing artificial materials from viscose, which comprises causing a viscose, prepared from an alkali cellulose which has been allowed to mature from naught to 48 hours, which viscose contains not more than 5 per cent of caustic alkali (calculated as NaOH), to pass through suitably formed openings into a coagulating bath containing not less than 45

but less than 55 per cent of sulphuric acid monohydrate and stretching the coagulated material in the coagulating bath and between the coagulating bath and the collecting device.

20. Process for manufacturing artificial materials from viscose, which comprises causing a viscose, prepared from an alkali cellulose which has been allowed to mature from naught to 48 hours, which viscose contains not more than 5 per cent of caustic alkali (calculated as NaOH), to pass through suitably formed openings into a coagulating bath containing not less than 45 but less than 55 per cent of sulphuric acid monohydrate and heating the artificial material after washing and drying it.

In testimony whereof I affix my signature.

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