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METHOD FOR TREATING NATURAL AND ARTIFICIAL SILK AND PRODUCTS OBTAINED THEREBY

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The present invention is an improvement over the process and products described in the former application for Letters Patent of the United States, filed by one of us under Serial No. 425,707 on February 3, 1930, and entitled "Process for treating fibers and product obtained thereby".

The process of this prior application has particularly for its object to find a way by which both natural and artificial silk may be quickly weighted with less labor, less danger to the operator and with less injury to the produced goods. Under artificial silk we understand any fiber which either entirely or partly consists of cellulose regenerated from a cellulose solution, such as viscose silk, cuprammonium silk, such made from zinc-chloride cellulose solutions, or which consists of a cellulose ester, such as cellulose acetate, cellulose nitrate in its pure or denitrated forms, cellulose formates, or of cellulose ethers, or of one of the other varieties occasionally suggested.

This aforesaid purpose was satisfactorily accomplished by means of a weighting solution, made by dissolving a rare earth metal carbonate, for instance such as lanthanum, didymium, thorium etc., according to the equations

1. $SnCl_4+La_2(CO_3)_3+6H_2O=3SnCl_3\cdot OH\ La_2Cl_3(OH)_3+3CO(OH)_2$

2. $3H_2\cdot CO_3=3H_2O+3CO_2$.

The silk was treated with the weighting solution, thus obtained, and after being washed with water, the silk was then treated with a solution of a salt, giving with the tin and the rare earth metal an insoluble salt.

In connection with the newly found weighting solution it was described in aforesaid application, Serial No. 425,707, for which reason this new weighting solution was superior to the solution of tin tetrachloride applied exclusively in the weighting of silk for almost 50 years.

Owing to the corrosiveness of this solution to the hands of the operators and the utensils needed in the dyeing process and to the destruction the deposited tin compounds gradually exerted upon the silk fiber, the silk dyers and consumers have made many efforts to overcome the weak points of weighting silk with tin-tetrachloride solution.

In view of the properties of tin-tetrachloride, the sensitiveness of the natural and artificial silk fibers, and particularly of the costliness of these materials, the making of extensive experiments is a rather delicate affair; therefore, also in the process of the application #425,707 all circumstances surrounding the same could not be ascertained at once, even though the investigation of the process described by the said application was a most careful and minute one. It required further extensive experiments and a great line of analytical work to more explicitly disclose all the merits of the technical proposition to weight natural and artificial silk with a deacidified solution of tin-tetrachloride.

Though theoretically tin-tetrachloride is a neutral substance, it actually displays in its various applications a rather acid character; it has, however, more than any other substance the capacity to undergo hydrolysis when absorbed by the silk fiber with the result that basic tin-chloride salts are formed and as the tin salt is retained by the fiber, the hydrolysis of the tin-tetrachloride is greatly accelerated by washing the silk fiber with water.

To whatever reason it may be due that weighting artificial silk up to now is an unknown art (see "Artificial Silk" by Hottenroth, 1928, page 369, published by Sir Isaac Pitman & Sons, Ltd., London), it can, as already described in application, Serial No. 425,707, be done with a solution of tin-tetrachloride deacidified with a carbonate of one of the rare earth metals so as to contain basic chlorides of both tin and of the rare earth metals.

It is now the object of the present invention to provide a process for weighting natural and artificial silk with tin-tetrachloride deacidified with carbonates of other metals, than the rare earth metals with mixtures of carbonates of such other metals, and with mixtures of carbonates of such other metals with such of the rare earth metals.

In investigating the effect of a tin-tetrachloride solution, deacidified with the carbonate of such other metals alone or with those of the rare earth metals, we found not only that natural and artificial silk suffer less than by other treatments, but that they also take up more weight in the subsequent washing.

While more closely investigating the relation between tin-tetrachloride and the carbonates of such other metals with or without those of the rare earth metals, respectively, and further investigating the effect of the solution of the basic tin-tetrachloride and the basic metal chlorides obtained in the aqueous solution by the interaction of the aforesaid substances, we found that the natural silk was heavier weighted than when treated as usually under the same conditions with a solution containing $SnCl_4$ only, the presence of such other metal compounds, forming highly insoluble salts with alkali metal silicates, phosphates, tungstates or other similar soluble salts, even if these per se displayed little inclination to precipitate upon and to be absorbed directly as an insoluble salt by the silk, caused the corresponding insoluble tin salt to do so in a greater degree.

In other words: The presence of the other metal compounds accelerates and favors the precipitation of the tin-oxyhydrate upon both natural and artificial silk.

We found that this accelerating action is noticeable with all those weighting solutions made by dissolving in the tin-tetrachloride solution the carbonate of a metal, the chloride of which is readily soluble in water, but the phosphate of which is insoluble.

One of the prime requirements of the aqueous tin-tetrachloride solution, deacidified by the carbonate of a metal forming a soluble chloride and an insoluble phosphate, is that the solution be clear and colorless and remain free of any sediments, or precipitations to whatever cause they may be due; this we found to be the case with all metals, the chlorides and phosphates of which fulfill the aforesaid conditions of solubility.

Moreover, we found that the addition of an organic acid, forming a soluble iron salt, but an insoluble cerium salt, for instance such as formic acid, or citric acid, exerts a beneficial effect and contributes largely to the durability of the solution.

If solutions of the character, as pointed out above, are applied to artificial silk it is absorptive enough to be as highly weighted as natural silk.

A glance upon the tables given below shows not only a considerable increase in weight, but it also shows the important fact that the high atomic weight is not so much the determining factor, but the readiness with which the added carbonates dissolve in the concentrated tin-tetrachloride solution to form a stable solution of relatively great durability and of high specific gravity. In conformance herewith we may state that the carbonates of magnesium and zinc are especially suitable for the preparation of strongly basic and highly durable colloidal tin-chloride solution from $SnCl_4$.

The chlorides of magnesium and zinc are highly soluble and their phosphates are insoluble in water, their phosphates having furthermore a very advantageous property in so far that they have a soft, velvet-like feeling. In further evidence of the fact that the solubility of the chloride and the insolubility of a metal phosphate are the determining factors of whether or not its basic chloride together with those of tin make a good weighting solution, we cite for instance lithium as an example, which has the very low atomic weight of 7, but which, if applied in conformance with the present invention, causes the silk, or artificial silk to take up a surprisingly high weight.

The weighting solutions made according to our new process have another remarkable advantage over the plain tin-tetrachloride solution of the prior art.

The weighting of silk was usually performed in the prior art in dark rooms, for instance in cellars, or other rather insufficiently lighted spaces so as to particularly exclude the effect of the sunlight. Silk weighted and phosphated in the sunlight inclined very much to deterioration, but this is not noticed when natural silk, or the even more sensitive artificial silk, is treated with a weighting solution according to our present invention.

To produce this weighting solution we introduce from 100–125 gr. of a metal carbonate, the chloride of which is soluble and the phosphate of which is insoluble, into 750 gr. of a tin-tetrachloride solution of 50° Bé., heated to 70–75° C.; for instance we introduce 100 gr. zinc carbonate into the above mentioned quantity of tin-tetrachloride. When the amount of 100–125 gr. of metal carbonate is introduced into the tin-tetrachloride, the solution thus ultimately obtained shows usually a practically neutral reaction. Finally we add to the solution about 10 gr. of concentrated formic acid, citric acid, or acetic acid etc. and dilute the same until it shows 31 Bé.

The carbonates of other metals coming in consideration for the application of our process are those of the following: lithium, barium, calcium, magnesium, strontium, cadmium, copper, iron, chromium, uranium, lead, bismuth, zirconium, titanium, either alone or in mixture. Moreover, the carbon-

ates of aforesaid metals may also be applied in combination with one or more of those of the rare earth metals, such as cerium, lanthanum, neodymium, samarium, didymium, thorium, scandium, yttrium, praseodymium, terbium, europium, gadolinium, ytterbium and other representatives of the group.

The obtained solution is allowed to stand to settle out any undissolved particles and the clear part is removed either by decantation or filtration, whereupon the solution is ready for immediate application.

For example: Having deacidified the tin-tetrachloride solution by zinc carbonate, the silk, which was first degummed, or artificial silk, such as made of viscose, is allowed to soak for some time, for instance 1–1½ hours, in the obtained solution of basic zinc-tin chloride; it is then taken out, the surplus of the solution is thoroughly squeezed out of the silk or viscose silk, and the same is then washed with little water. The washed silk is then introduced into a solution of a metal salt giving by double decomposition with the tin compound in the fiber an insoluble salt; such a solution is for instance that of an alkali-metal phosphate, such as a di-sodium phosphate bath, having a temperature of 70° C.

The silk or viscose silk is allowed to hang therein also for 1–1½ hours; when taken out it is washed and dried. This procedure may be repeated once or twice, or as often as desired; it is repeated twice in all cases for the purposes of comparing the results of this invention in its operation with the various salts and with the process of the prior art of alternately soaking the silk in the tin-tetrachloride solution and phosphating it three times.

Below we give a table of the ultimate results of our process by indicating the total increase in weight with weighting solutions, containing the basic chlorides of various metals, in comparison with the treatment with tin-tetrachloride only, the alternate soaking in each weighting solution and in the phosphating bath being operated altogether three times to put the examples on the same basis.

Table I

	Weighting solution of the chlorides respectively basic chlorides of the following:	Total increase in weight
(a) Silk	Tin	51.136%
(b) Same	Lead-tin	60.00 %
(c) Same	Zinc-tin	66.30 %
(d) Same	Zirconium-tin	68.47 %
(e) Same	Neodymium-magnesium tin	72.72 %
(f) Viscose silk	Zinc-tin	84.34 %
(g) Same	Magnesium-tin	86.66 %

In the table below we show how steadily in some of the above examples the weight of silk, or artificial silk (viscose silk) increases with each alternate soaking in the weighting solution and in the phosphating bath.

Table II

Weight in grams	Original	After 1 soak.	After 1 phosph.	After 2 soak.	After 2 phosph.	After 3 soak.	After 3 phosph.	Example in Table I
Increase %	44	49.50	51.00	57.50	59.50	62.50	66.5	
		12.50	15.90	29.545	35.22	42.05	51.14	a
Increase %	45	51.00	53.00	60.00	63.00	68.00	72.00	
		13.53	17.78	33.33	40.00	51.11	60.00	b
Increase %	46	51.50	53.00	62.00	65.00	73.50	76.50	
		11.96	15.22	34.78	41.30	58.70	66.30	c
Increase %	57.50	77.00	77.00	91.50	91.00	100.50	106.00	
		33.91		57.39	------	74.78	84.34	f
Increase %	60.00	75.50	79.50	91.00	93.00	107.50	112.00	
		25.83	32.50	51.66	55.00	79.17	86.66	g

For the deacidification of the tin-tetrachloride solution it is by no means necessary to apply exclusively the carbonate of the various metals pointed out above; any other of their basic compounds, for instance the hydrates of the metals forming a hydroxide insoluble in water, but forming a soluble chloride and an insoluble phosphate, such as zinchydroxide, magnesium hydroxide, aluminum hydroxide, stannichydroxide, the hydroxides of the rare earth metals etc. may be applied with like success; also certain salts, in which the metal oxide, contained therein, displays an acid character, for instance sodium zincate, sodium plumbate, sodium aluminate, sodium stannate, etc. may be applied with good success, because by interaction with acid the respective metal hydroxides are formed.

Though in connection with weighting natural or artificial silk, the idea suggests itself that the insoluble precipitate of the metal compounds on such natural or artificial silk, be white, we wish to point out that also metals forming a colored phosphate, tungstate etc. are falling within the scope of our invention. If natural or artificial silk is to be dyed in dark shades, insoluble metal salts of dark colors are very desirable in the weighting of the silk, as a pretreatment for, or part of the dyeing process.

The operation of the process with any of the weighting solutions, made according to the directions given above, is very simple and can be performed by a working man without chemical training; this is facilitated by the fact that the highly concentrated solutions are always clear and stable and may be kept without any appreciable losses.

Though we have reason to believe that the fact of the high weighting of silk by the weighting solutions described above may be due to the transfer of part of the original amount of acid from and the tin to the other metal added thereto and that owing to the formation of basic salts hydrolysis is facilitated, we have no information sufficient to

reliably explain the phenomena which may occur in the weighting of artificial silk.

We furthermore wish to state that we have enumerated the metals exclusively from the standpoint that they answer the requirements of our process and have disregarded, as in the case of lead, that one or the other, owing to its poisonous character, might not be suitable for certain purposes, for instance for weighting silk for wearing apparel.

Finally we wish to say that the essential features of our new weighting process may also be attributed to other metal salts known as suitable for weighting silk, for instance to zirconium chloride, titanium tetrachloride etc., which may take the place of the tin-tetrachloride in our process; of these other weighting metals particularly the salts of titanium, such as its tetrachloride, or sulfate, are very suitable for this purpose.

For example titanium tetra chloride possesses also the disadvantage that it hydrolyzes strongly in aqueous solution and therefore considerable quantities of free acid are separated out, which acid has a disadvantageous effect on the degree of weighting the fiber, its feel and durability when finished.

By our invention this acid, which in the processes of the prior art separates out, is in our process destroyed by binding it with the basic compound of another metal which per se must not necessarily be a metal having a high "weighting" effect. We are aware that processes have been suggested to counteract the disastrous effect of the acid separated out, for instance from titanium tetrachloride, but to our knowledge none of these processes accomplishes this end by neutralizing the liberated acid.

Aforesaid remarks about titanium and zirconium salts as "weighting" materials to take the place of tin salts bear particularly on weighting natural silk and artificial silk for white and light colors; the statements, made in regard to them hold also good of other salts, so of aluminum salts and particularly for iron, chromium and other similar metal salts which are at present applied for weighting silk to be dyed with dark shades. It is obvious that aforesaid weighting metals have a double function; namely, in one case they can act as the chief weighting metal and in the other case their basic compounds may be resorted to for deacidifying the solutions of tin or other weighting metal salts.

We have stated above that the presence of such other basic metal compounds in the deacidified tin-tetrachloride solution is desirable, which by interaction with an alkali metal silicate, an alkali metal phosphate or alkali metal tungstate or similar alkali metal salts form an insoluble salt. We are aware that we have chosen the action with an alkali metal phosphate as an example of the operation of our new process; we gave these examples because we found it good practice to form first a deposit of tin and other metal phosphates on the fiber and to eventually subsequently deposit the tin and other metal silicates or metal tungstates, etc. on the natural or artificial silk, by which statement, however, we do not want to restrict ourselves to this line of steps and we claim alkali-metal silicates, tungstates, molybdenates etc. as full equivalents to the alkali metal phosphates in their effect.

Accordingly we embrace all these alkali metals salts mentioned in the last sentence in the term "alkali metal salts containing an acid metal oxide" there being no exact limit between metals and non metals.

Finally we wish to state that our process applies alike to natural and artificial silk in the piece as well as in the skein. In the latter case it is of importance that though in the course of the operation of our process the Baumé degree of the weighting solution may get lower, still the goods always draw a practically equal amount of metal from the same so as to furnish particularly also piece goods of an even weighting.

Whenever we speak of an alkali metal salt for acting on the basic tin and other basic metal salts, we also mean to include the corresponding ammonium salt in the term "alkali metal salt".

What we claim is:

1. As a base for weighting both natural and artificial silk fibers, an aqueous solution of the basic chlorides of tin and of a metal, other than a rare earth metal, said latter metal forming a soluble chloride and an insoluble phosphate.

2. As a base for weighting both natural and artificial silk fibers, an aqueous solution of the basic chlorides of tin, of a rare earth metal and of a metal, other than a rare earth metal, said latter metal forming a soluble chloride and an insoluble phosphate.

3. As a base for weighting both natural and artificial silk fibers, an aqueous solution of a basic tin chloride and basic zinc chloride.

4. As a base for weighting both natural and artificial silk fibers, an aqueous solution of a basic tin chloride and basic magnesium chloride.

5. As a base for weighting both natural and artificial silk fibers, an aqueous solution of a basic tin chloride and the basic chlorides of magnesium and of neodymium.

6. The process of weighting both natural and artificial silk fibers, consisting in acting on the fiber with the aqueous solution of basic chlorides of a plurality of weighting metals other than rare earth metals, then washing the fiber with water, and subjecting the fiber thus treated to the solution of a salt capable

of forming an insoluble salt with the metals of the salts of aforesaid aqueous solution.

7. The process of weighting both natural and artificial silk fibers, consisting in acting on the fiber with the aqueous solution of basic chlorides of a plurality of weighting metals other than rare earth metals, then washing the fiber with water, and subjecting the fiber thus treated to the solution of an alkali metal salt capable of forming an insoluble salt with the metals of the salts of aforesaid aqueous solution.

8. The process of weighting both natural and artificial silk fibers, consisting in acting on the fiber with the aqueous solution of the basic chlorides of tin and of a weighting metal other than a rare earth metal, then washing the fiber with water, and subjecting the fiber thus treated to the solution of a salt capable of forming an insoluble salt with the tin and the other metal of the salts of aforesaid aqueous solution.

9. The process of weighting both natural and artificial silk fibers, consisting in acting on the fiber with the aqueous solution, of a basic chloride of tin and of the basic chlorides of a plurality of other weighting metals, one of them being a rare earth metal, then washing the fiber with water, and subjecting the fiber thus treated to the solution of a salt capable of forming an insoluble salt with the metals of the salts of aforesaid aqueous solution.

10. The process as described by claim 8, said process comprising acting on the solution of a tin-tetrachloride with the basic compound of a weighting metal other than a rare earth metal and capable of forming a soluble chloride and an insoluble phosphate, thereby generating basic chlorides of tin and of the other metal within the solution, and then acting upon the fiber with said solution.

11. The process as described by claim 8, said process comprising acting on the solution of tin-tetrachloride with the carbonate of a metal other than a rare earth metal and capable of forming a soluble chloride and an insoluble phosphate, thereby generating basic chlorides of tin and of the other metal within the solution, and then acting upon the fiber with said solution.

12. The process as described by claim 9, said process comprising acting on the solution of tin-tetrachloride with the carbonate of a metal of the group of the rare earth metals and that of another metal outside aforesaid group and capable of forming a soluble chloride and an insoluble phosphate, thereby generating basic chlorides of tin and of the other metals within the solution, and then acting upon the fiber with said solution.

In witness whereof we have hereunto set our hands.

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