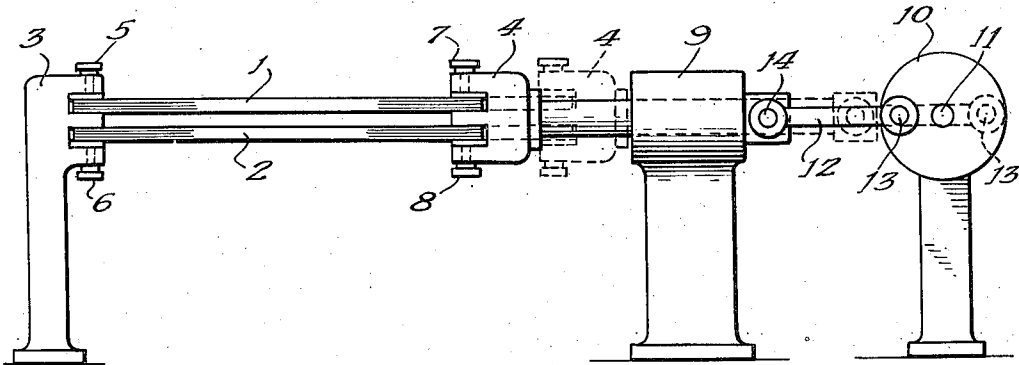


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PREPARATION OF PROTEIN COMPOSITIONS AND MASSES
HAVING IMPROVED PHYSICAL CHARACTERISTICS
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PREPARATION OF PROTEIN COMPOSITIONS
AND MASSES HAVING IMPROVED PHYSICAL CHARACTERISTICS

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18 Claims. (Cl. 18-48)

This invention relates to the preparation of protein compositions and masses having improved physical characteristics, and is a continuation in part of my co-pending application Serial No. 480,586, filed March 25, 1943.

It is well known that proteins may possess considerable resiliency, and that this resiliency may be further enhanced by the incorporation of plasticizers. Such plasticized protein masses, however, have a very low melting point, which is frequently objectionable. This melting point is raised by tanning agents, such as, for example, lower aldehydes, quinones, salts of chromium, iron, aluminum and the like, tannic acid and the like, triethanolamine, sulfonated compounds such as sulfonated oils, sulfonated succinyl esters, et cetera. However, such tanning agents also cause a rapid loss of elasticity and destroy or greatly impair the tensile strength of resilient protein compositions.

An object of this invention is to provide protein compositions having a higher melting point concurrent with retained elasticity, than has been possible heretofore, articles of manufacture comprising such compositions, and methods for preparing them.

Further objects and more specific embodiments will become apparent as the following detailed description proceeds.

I have discovered that when a resilient protein composition is rhythmically stretched and relaxed while under the influence of an organic tanning agent, the melting point of the composition will increase about as much as would be the case if no such stretching took place, but the loss of the tensile strength will be substantially reduced, frequently entirely eliminated, and in some cases increased, both in the direction of the stretch and in directions perpendicular thereto.

This effect is thoroughly different in kind from the increase in tensile strength in stretching of rayon filaments, which is due to an orientation of molecules in the direction of stretch. The effect here disclosed takes place only in the presence of an organic tanning agent, only when stretching is carried out concurrently with an increase in melting point caused by this tanning agent, and the effect takes place in directions perpendicular to the stretching as well as in the direction of the stretch.

The following example will serve to illustrate this invention, reference being had to the accompanying drawing which shows a diagrammatic view of a reciprocating device for stretching and relaxing the sheets:

300 grams of 225 Bloom pig skin gelatin was allowed to swell in a mixture of 300 grams of glycerol and 450 grams of water, at room temperature. After one hour, the mixture was melted in a water-bath of 55° and mixed with 1500 grams

of additional glycerol, pre-warmed in the same water-bath.

The resultant mix was divided in two 50% aliquots. To one of these I added 60 cc. of 33% acetaldehyde solution, as tanning agent; the other aliquot served as my non-tanned control.

The mixes were allowed to stand one-half hour at 55° to eliminate air bubbles, and were then poured to form uniform sheets having the dimensions 330 mm. x 216 mm. x 2.5 mm. Two such sheets were obtained from each aliquot. The sheets were allowed to stand for twenty hours at room temperature in order to give them the firmness required.

After this period, one tanned sheet 1 and one non-tanned sheet 2 were attached with one short end to a rigid metal holder 3, and with the other short end to a holder 4 having a reciprocating motion, so that the sheets were continually stretched and relaxed at a rate of eight times per minute, to an extent of 10% elongation.

The sheets 1 and 2 are clamped in the holders 3 and 4 by means of screws 5, 6, 7 and 8. The reciprocating motion is provided by a disk 10 rotating on shaft 11 by means not shown. An arm 12 is pivoted at 13 and 14 and connected to the holder 4 by a sliding shaft mounted in support 9, whereby on rotation of the disk 10 holder 4 reciprocates and thus stretches and relaxes the sheets 1 and 2.

The other two sheets, one tanned and one non-tanned, were placed on a porous backing next to the stretching machine, and were thus exposed to room temperatures, humidities and ventilation identical with those of the stretched samples.

After twelve days, the stretching was interrupted, the sheets were kept overnight (sixteen hours) at 55% relative humidity and 21°. Test strips were cut from center and ends of each sheet having their length parallel to the direction of stretch, and others perpendicular thereto, and the tensile strength was determined in a conventional paper tensile strength testing machine.

The tabulated figures are averages of triplicate determinations, all of which were within 5% of the averages shown.

TABLE

Tensile strength in grams per sq. mm.

		In direction of stretch	Across direction of stretch
Stretched tanned sheet	(End	171	144
	(Center	192	146
Stretch non-tanned sheet	(End	153	148
	(Center	150	152

Tanned non stretched sheet, 60
Non-tanned non stretched sheet, 155

With the stretched sheets, determinations were

made at the end and the center of each sheet, as the direction of stretch might have shown slight deviations near the edges.

The most striking facts shown by these data are: (I) that the stretched tanned sheet not only is vastly stronger (320%) than the non-stretched tanned sheet in the direction of stretch, but also in the direction of perpendicular to the tension (240%); (II) that the stretched tanned sheet is materially stronger in the direction of stretch than is the non-tanned sheet; (III) that in the non-tanned sheets there is no correlation between strength and direction of stretch, while in the tanned sheets this correlation is pronounced; (IV) that in the non-tanned sheets, stretching did not cause any observable increase in strength.

Since the strength of the stretched tanned sheet was several times greater than that of the non-stretched tanned sheet, it appeared advisable to investigate whether the tanning itself had been impeded by the stretching process. For this purpose, the softening points of the sheets were determined on circular samples of 25 mm. diameter, by the ring and ball method, in oil-bath.

The softening points of both of the non-tanned sheets were $60^{\circ} \pm 1^{\circ}$, while those of the stretched as well as the non-stretched tanned sheets exceeded 110° C .

The elongation of the stretched sheets at the termination of the test was approximately 5%, and was thus insignificant in relation to the effects observed.

The same effect was found to occur in any stretchable protein gel, under the influence of organic tanning agents. Proteins tested include gluten, gelatin, edestin, zein, zeinin, salmin, glue, gliadin, soybean protein, peanut protein, blood albumin, casein and eggwhite, and combinations thereof.

Plasticizers tested include glycerin, ethylene glycol, sorbitol, mannitol, glucose, saccharose, ethylene glycol, monoethyl ether, urea, thiourea, tetraethylene glycol, ethyl sulfonamide, urethane, propylene glycol, formamid, diethylene glycol, polyglycerols, acetamid, toluene sulfonamid, dibutyl tartrate, and the like.

Suitable tanning agents include formaldehyde, acetaldehyde, butyraldehyde, crotonaldehyde, tannic acid, parabenzquinone, hydroquinone, triethanolamine, organic substances containing a free sulfonic acid group, and generally any organic substance capable of reacting simultaneously with any free groups in two different protein molecules, so as to form a bridge between these protein molecules. Generally, I prefer to employ for the purposes of the invention an aldehyde having less than five carbon atoms, or a quinone derivative having tanning action, although any other of the organic compounds disclosed may be used.

Much shorter times of stretching than those stated above will suffice to increase the strengthening of the gels, particularly if tanning is speeded concurrently by the use of more potent tanning agents, so that tanning is substantially completed while the stretching and relaxing action takes place.

For example, if a strong tanning agent, such as, for example, a bath of several percent, say .1 to 5% of formaldehyde or .5 to 10% of acetaldehyde or of parabenzquinone is used in acid, neutral or alkaline solution, then the effect may be attained in a matter of seconds, by stretching

and relaxing as few as 20 to 100 times at a very rapid rate, for example with a holder, or by passing over rollers given a short swing reciprocating motion by means of a vibrator. Preferably the filament or film so stretched is left intact and is not cut or severed so that no curling or similar appreciable permanent deformation takes place.

The increases in strength thus obtained are generally not so large as those described in the first example, but are generally quite observable, amounting to as much as 1 to 5%, and more.

Fundamentally, the invention comprises an increase in strength effected by several times repeated stretching and relaxing while progressive tanning is taking place and without any appreciable concurrent bending or curling.

As for practical applications, I contemplate the protein gels described as such, as new and useful raw materials having a materially higher elasticity concurrent with materially higher melting point than has heretofore been possible in the same compound. I further contemplate sheets or other formed articles made from such products, which may include "cellophane" like sheets as well as more plastic printing rolls or hectograph blankets; furthermore protein textile filaments or artificial fibers having a much higher resiliency and tensile strength than has heretofore been possible may be made and woven into fabric. Suitable compositions are prepared according to the invention by exposing the protein compositions after they have been poured or extruded, and after the tanning agent used has been incorporated, but before they have attained their final hardness or rigidity to a rhythmical stretching and relaxing action. This is accomplished easily by passing the material in the form of a sheet, filament or the like over rollers, belts, reels or the like, of which every other revolves at a lower and every other at a higher speed, so that a slack is formed between every other pair of rollers and a tension between every other pair. Obviously, the desired result is accomplished by any other means for alternately stretching and relaxing the material produced while this is being hardened by the action of the tanning agent.

In the manufacture of hectograph blankets the hectograph gel formed, for example, of a usual gelatin-glycerin-water-aldehyde composition may be made in the form of a continuous ribbon without contact with a backing. This gel ribbon is stretched and relaxed while hardening takes place, due to the action of the tanning agent. This treated gel is then secured to a backing in a separate operation to form a hectograph blanket of the usual type which is adapted to be wound into a roll.

In one method of manufacturing hectograph blankets the hectograph composition in its fluid state is applied under a scraper blade to a continuous belt which is impregnated for example, with paraffin wax, or with some other material to which the mass will not bond. The belt is of such length that the composition is completely set to a gel at the end remote from the application of the composition. From this end of the belt the gel itself is carried over a series of rollers in a festoonlike arrangement so that every other roller would revolve at a high speed and every other roller at low speed. In this manner the mass is stretched between every slow revolving roller and every fast revolving roller and relaxed between every fast revolving roller and slow revolving roller, so that a continuous stretching

and relaxing takes place. Upon completion of the treatment the band of hectograph mass is slit and cut to pieces of appropriate size and bonded to the backing material by suitable means such as by any of the various bonding agents for bonding hectograph masses to backings.

The invention manifestly is capable of wide variation, and the examples and expedients suggested by way of illustration should not be construed to limit the disclosure.

It will be understood that in order to attain the improved physical characteristics in a reasonable period of time (less than one month) so as to have a commercially practical process the protein composition should be stretched a substantial distance such as to 5% or 10% elongation, and the stretching over a substantial distance, followed by relaxation should preferably be repeated at a rate of several times per minute on a protein composition containing an organic tanning agent, which composition is still in the process of undergoing tanning and capable of undergoing substantial further tanning.

I claim:

1. The method of improving the physical characteristics of a protein mass which comprises alternately stretching and relaxing said mass at least about 20 times while said mass is under the influence of a tanning agent.

2. The method of improving the physical characteristics of a gelatin mass which comprises alternately stretching and relaxing said mass at least about 20 times while said mass is under the influence of a tanning agent.

3. The method of improving the physical characteristics of a protein gel containing an organic tanning agent which comprises alternately stretching and relaxing said gel at least about 20 times while said gel is undergoing tanning.

4. The method of improving the physical characteristics of a protein gel containing an organic tanning agent which comprises alternately stretching and relaxing said composition through a substantial distance of extension at least about 20 times while said gel is undergoing tanning.

5. The method of improving the physical characteristics of a protein gel containing an organic tanning agent and a plasticizer, which method comprises alternately stretching and relaxing said gel at least about 20 times while said gel is undergoing tanning.

6. The method of improving the physical characteristics of a protein gel containing an organic tanning agent, water and a less volatile plasticizer, which method comprises alternately stretching and relaxing said gel by means of a vibrator at least about 20 times while said gel is undergoing tanning.

7. The method of improving the physical characteristics of a protein gel containing an organic tanning agent having a liquid disperse phase greater than the solid dispersed phase, which method comprises alternately stretching and relaxing said gel at least about 20 times substantially before said gel has completely reacted with said tanning agent, substantially without causing any permanent deformation of said gel.

8. The method of improving the physical characteristics of a formed article of manufacture made from a protein composition which comprises alternately stretching and relaxing said formed article at least about 20 times while subjecting the protein of said article to the action of an organic tanning agent, without causing any appreciable permanent deformation of said gel.

9. The method of producing a tanned protein composition having improved tensile strength which comprises incorporating an organic tanning agent in a protein composition and alternately stretching and relaxing said composition at least about 20 times concurrently with the increase in melting point of said gel caused by said tanning agent, without causing any appreciable permanent deformation of said gel.

10. The method of producing a tanned, plasticized gelatin mass having improved tensile strength, which method comprises mixing together gelatin, water, a less volatile plasticizer, and an organic tanning agent to obtain a composition which will form a sol at an elevated temperature and a gel on cooling, pouring said composition at an elevated temperature in its sol state on a surface, allowing the sol to cool and set to a gel, removing the gel in the form of a sheet from the surface, and alternately stretching and relaxing said gel sheet at the rate of several times per minute to extent of at least about 10% elongation for several days.

11. The method of making a formed article of protein having improved physical characteristics which comprises incorporating an organic tanning agent in a protein composition, forming said composition into an article of manufacture, and alternately stretching and relaxing said article at least 20 times before said tanning has brought about final hardness.

12. The method of making a protein sheet having improved physical characteristics which comprises incorporating an organic tanning agent in a protein composition, forming said composition into a sheet, and alternately stretching and relaxing said sheet at least 20 times before said tanning agent has brought about final hardness.

13. The method of making a hectograph blanket having improved physical characteristics which comprises forming a hectograph copy mass comprising a protein gel containing an organic tanning agent, and alternately stretching and relaxing said gel at least 20 times before said tanning agent has brought about final hardness.

14. The method of making protein filament having improved physical characteristics which comprises incorporating an organic tanning agent in a protein composition, forming said composition into a filament, and alternately stretching and relaxing said filament at least about 20 times before said tanning agent has brought about final hardness, without causing any appreciable permanent deformation of said filament.

15. A tanned protein composition in the form of an artificially shaped mass obtained by alternately stretching and relaxing said mass at least 20 times during tanning by means of a vibrator, said mass being characterized by having substantially greater elasticity and tensile strength than a mass of a tanned protein composition of the same chemical compounding and tanning.

16. An artificial textile filament made in accordance with the process of claim 14.

17. A woven fabric comprising the fiber made in accordance with the process of claim 14.

18. The method of improving the physical characteristics of a protein filament which comprises alternately stretching and relaxing said filament at least about 20 times while said filament is under the influence of a tanning agent.

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