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METHOD OF DISPERSING KERATIN PROTEIN WITH AMMONIUM THIOCYANATE AND THE COMPOSITION RESULTING THEREFROM

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This application is made under the act of March 3, 1883, as amended by the act of April 30, 1928, and the invention herein described, if patented, may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment to us of any royalty thereon.

This application is a division of our copending application for patent, Serial No. 562,326, filed November 7, 1944.

This invention relates to a method of dispersing keratin proteins obtained from a keratin material such as feathers, hoofs, horns, wool, and so forth, and has among its objects the use of such keratins, either in the dispersed or recovered forms, in the preparation of artificial fibers, films, plastics and the like.

Keratins, like the more soluble proteins, can be readily dispersed by hydrolysis in strong acids or alkalis, but the keratin thus dispersed cannot be recovered except as simple degradation products, such as amino acids or complex degradation products, such as peptides, peptones, and proteoses, the properties of which differ radically from those of the original keratin.

Keratins can also be dispersed in alkaline solutions of metallic sulphides and such sulphides are commonly used in cosmetic depilatories and in the removal of hair from hides in the tanning industry.

Keratins have also been dispersed at neutral reactions but in these cases heat and high temperatures were employed to the point of charring, which produced drastic degradation of the proteins.

Also, keratins may be dispersed in strong alkaline solutions by treatment with reducing agents, and the recovered protein is more similar to the original protein in regard to solubility, molecular size, and so forth, than are the peptides, proteoses, etc., referred to previously. However, the presence of the strong alkali is undesirable because it presents an opportunity for the hydrolysis of the keratin, destruction of the cystine constituent of the keratin (keratins being unique among proteins in that they contain exceptionally large amounts of cystine), and destruction of the hydroxy amino acid residues of the keratin.

According to our invention, keratin materials are dispersed under mild conditions, that is, in

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neutral or practically neutral reaction, and at relatively low temperatures. These conditions produce less degradation of the original keratin than occurred in the prior art and the dispersed keratin may be recovered in a form substantially similar to that of the original keratin in regard to its composition, isoelectric point, solubility, and other properties.

The method involved in this invention is based partly on the reduction of the disulphide bonds within the keratin molecule by treating it with sulfur-containing, reductive disulphide-splitting agents such as monoethylene thioglycol (thioglycol), thioglycolic acid (present as the thioglycolate in neutral solution), and sodium bisulphite.

The presence of alkali is obviated by the use of any of a number of protein-denaturing or protein-dispersing agents, such as urea, guanidine hydrochloride, ammonium thiocyanate, formamide, acetamide, thiourea, sodium salicylate, urethane, phenol, lithium iodide, and surface-active agents, such as synthetic detergents composed of sodium alkyl aryl sulfonates, sodium alkyl sulfates, and so forth, and dispersion of the keratin is thus effected at neutral or practically neutral reaction.

Therefore, under the above conditions of employing disulphide-splitting and protein-dispersing or protein-denaturing agents to effect the dispersion in neutral or practically neutral reaction and at relatively low temperatures, the keratin molecule undergoes minimal degradation, the only chemical attack on the covalent linkages of the keratin being the cleavage of the disulphide bonds of the cystine moiety.

The following examples are illustrative of our invention:

Example I

1.4 parts of monothioethylene glycol and 27.2 parts of guanidine hydrochloride are dissolved in water. Sodium hydroxide solution and water are then added as required to obtain 35 parts of solution at about pH 6.9. 2.5 parts of cattle hoof filings are treated with this neutralized solution in a water bath at about 40° C. about for 18 hours. The mixture is stirred at convenient intervals. During this period about 74% of the hoof keratin is dispersed in the solution. After removal of the undispersed hoof by filtration, the dispersed

keratin may be precipitated either by dilution with several volumes of water, by salting out with $MgSO_4$, $(NH_4)_2SO_4$, etc., by acidification, or by dialysis. If desired, the guanidine may be removed from the dispersion by dialysis and may be recovered from the dialysate by precipitation as the nitrate or by other suitable means.

Example II

1.1 parts of $NaHSO_3$ and 21 parts of urea are dissolved in water. Sodium hydroxide solution and water are added as required to obtain 35 parts of solution at about pH 7.1. 2.5 parts of wool are treated with this solution in a water bath at about 40° C. about for 18 hours, during which period the mixture is stirred at frequent intervals. 52% of the original weight of the wool is dispersed by this treatment. The dispersed wool may be precipitated and recovered from the solution either by dialysis, by salting out with $MgSO_4$, $(NH_4)_2SO_4$, etc., or by careful addition of a suitable amount of acid or alkali.

Example III

40 parts of a synthetic detergent composed of sodium alkyl aryl sulphonates, and 4 parts of $NaHSO_3$ are dissolved in water. Sodium hydroxide solution and water are added as required to obtain 400 parts of solution at about pH 6.6. This solution is heated to boiling and 64 parts of chicken feathers are added. The solution is kept boiling gently for about 30 minutes with frequent stirring. During this period considerable dispersion of the feathers occurs and the undispersed portion becomes very soft and loses its original shape. 200 parts of boiling water are now added and the solution is boiled and stirred for about another 30 minutes. The undispersed residue is removed by suitable filtration and is washed several times in hot water. The washings and filtrate may be combined and evaporated to dryness to obtain 70 parts of a water-soluble product that has been found useful for the preparation of artificial fibers. This material contains 8.5% to 8.6% nitrogen on a dry basis.

Example IV

50 parts of a synthetic detergent, composed of sodium alkyl sulphates, and 10 parts of $NaHSO_3$ are dissolved in 940 parts of water. A saturated solution of sodium hydroxide is added until the pH of the solution is about 6.0. The solution is heated to boiling and 80 parts of

chicken feathers are added. The solution is gently boiled for about one hour with frequent stirring. The undispersed residue is removed by suitable filtration and is washed several times in hot water. The combined washings and filtrate are evaporated to dryness. 75 parts of dry product are obtained having a nitrogen content of 8.5% to 8.6%. This material has been found useful for the preparation of artificial fibers.

Example V

1.6 parts of thioglycolic acid and 21 parts of urea are dissolved in water. Sodium hydroxide solution and water are added as required to obtain 35 parts of solution at about pH 7.0 (±0.2). 2.5 parts of duck feathers are added, and the mixture is heated at about 40° C. about for 18 hours. About 78% of the feather keratin is dispersed by this treatment.

Example VI

1.4 parts of monothioethylene glycol and 24 parts of ammonium thiocyanate are dissolved in water. Sodium hydroxide solution and water are added as required to obtain 35 parts of solution having a pH of about 6.9. 2.5 parts of chicken feathers are treated with this solution for about 18 hours at about 40° C. During this period about 82% of the feather keratin is dispersed.

Example VII

1.4 parts of monothioethylene glycol and 20.7 parts of acetamide are dissolved in water. Sodium hydroxide solution and water are added to give 35 parts of solution having a pH of about 7.2. 2.5 parts of chicken feathers are treated with this solution at about 40 C. about for 18 hours. During this period about 59% of the feather keratin is dispersed.

Example VIII

1.4 parts of monothioethylene glycol and 27.2 parts of guanidine hydrochloride are dissolved in water. Sodium hydroxide solution and water are added as required to obtain 35 parts of solution having a pH of about 7.0. 2.5 parts of hog hair are added and the mixture is heated at about 40° C. about for 18 hours. About 56% of the hair is dispersed during this period.

In addition to the foregoing examples, many other experiments were performed, the results of which are shown in the following tables:

TABLE I

Dispersibilities of keratins in different dispersing agents upon reduction by 0.5 M thioglycol

[2.5 g. of keratin was treated for 18 hours at about 40° C. with 35 ml. of solution at pH 7]

Keratin	Guanidine HCl (8.1 M)	NH_4CNS (9.0 M)	Formamide (10.0 M)	Acetamide (10.0 M)	Thiourea (1.2 M)	Synthetic [1] Detergent (10%)
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent* [2]
Chicken feather	84	82	66	59	10	79, 80
Duck feather	83	80	41	36	6	51, 53
Tortoise scutes	64	52				10, 8
Snake skin	55	44				26, 30
Cattle hoof	74	56	7	6	5	58, 64
Wool	61	36	4	6	4	44, 50
Cattle horn	36	27	3	5	4	14, 12
Hog hair	56	26	2	2	2	4, 3
Human hair	50	11	0	0	2	2, 1
Ovokeratin	8	6	4	3	15	2, 4

[1] Composed of sodium alkyl sulfates.
[2] First values calculated from dry weights of residues after acetone extraction; second values calculated from nitrogen analyses.

TABLE II

Dispersibilities of keratins in 10 M urea upon reduction by different disulphide-splitting agents

[2.5 g. of keratin was treated for 18 hours at about 40° C. with 35 ml. of solution at pH 7]

Keratin	Thioglycol (0.5 M)	Thioglycolic Acid (0.5 M)	$NaHSO_3$ (0.3 M)
	Per cent	*Per cent*	*Per cent*
Chicken feather	80	73	80
Duck feather	78	78	82
Tortoise scutes	52		
Snake skin	44		
Cattle hoof	30	23	39
Wool	27	29	52
Cattle horn	22	22	36
Hog hair	12	6	52
Human hair	4	5	26
Ovokeratin	2	2	5

Many changes and variations in the conditions for dispersion shown in the foregoing examples and tables may be made. As a rule, the higher the concentration of protein-dispersing or protein-denaturing agent, the greater is the percentage of keratin dispersed, the solubility of the dispersing or denaturing agent being a limiting factor. A greater degree of dispersion may also be obtained in some cases by increasing the concentration of the disulphide-splitting agent, as for example, for monoethylene thioglycol and thioglycolic acid. An increase in the concentration of $NaHSO_3$, however, often results in a decrease in the extent of dispersion of the keratin, presumably due to a salting-out effect.

Also, it is not necessary in every case that the solution be near the point of neutrality (pH 7.0). For example, the dispersibility of human hair in a solution of thioglycol and sodium salicylate is increased as the pH of the solution is increased about from 6.9 to 11.4. The use of neutral solutions merely minimizes the possibility of hydrolytic degradation of the protein which may be detrimental in some cases. If the pH is increased above about pH 10, dispersion occurs if only a disulphide-splitting agent is present; however, the presence of a protein-dispersing or protein-denaturing agent, as used in our invention, permits dispersion below pH 10.

The temperature at which dispersion, according to our invention, is obtained may range up to about 100° C., and the higher the temperature within this range, the shorter the time required for dispersion, and in some cases, a higher degree of dispersion is obtained. Therefore, it is recommended that the invention be conducted at a temperature range of up to about 100° C.

Having thus described our invention, we claim:

1. The process comprising heating a keratin material in an essentially neutral aqueous solution containing a sulfur-containing, reductive disulphide-splitting agent and ammonium thiocyanate at a temperature up to about 100° C. to disperse said keratin material in said solution.

2. The process comprising heating a keratin material in an essentially neutral aqueous solution containing monoethylene thioglycol and ammonium thiocyanate at a temperature up to about 100° C. to disperse said keratin material in said solution.

3. A composition of matter consisting essentially of a dispersion of a keratin material in an essentially neutral aqueous solution containing a sulfur-containing, reductive disulphide-splitting agent and ammonium thiocyanate.

4. A composition of matter consisting essentially of a dispersion of a keratin material in an essentially neutral aqueous solution containing monoethylene thioglycol and ammonium thiocyanate.

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