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COATED BOROHYDRIDES

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This invention is for improvements in or relating to borohydrides and for the use of these compositions, more in particular for the treatment of hair and processes for changing the configuration of hair.

The borohydrides frequently employed for the generation of nascent hydrogen are hygroscopic and inflammable compounds, and are analogous from this viewpoint to calcium carbide. They are difficult to handle, both in the laboratory, in which small quantities are dealt with, and a fortiori in industry, where greater quantities of these compounds are employed.

It is known that the configuration of hair may be changed, in the cold or with heating, i.e. at 10° C. to 100° C. by splitting the cystine linkages in the keratin structure and by reconstituting these linkages with the aid of an oxidizing agent, or more slowly with the aid of the oxygen of the air.

The splitting of the cystine linkages is effected by using reducing agents such as mercaptans or inorganic reducing agents, such as ammonium, sodium or lithium sulphites or bisulphites.

All of these reducing agents have disadvantages. The mercaptans can only be used in practice within limited pH values. If they are in a too alkaline medium, they act as depilatory agents, causing complete hydrolysis of the hair. Moreover, at the pH value at which they are normally used, their odor is disagreeable and they are not always well tolerated by the hair dresser or the persons to whom they are applied. Inorganic reducing agents generally do not penetrate well and, due to oxidation, they give bisulphates which are detrimental to the hair.

An object of the present invention is to provide a process for coating alkali metal borohydrides finely dispersed in an agent which is neutral with respect thereto and which facilitates the preservation and utilization thereof. A further object is to provide, as a new industrial product, a composition consisting of a homogeneous dispersion of alkali metal borohydrides in a neutral agent which ensures preservation and facilitates manipulation and utilization thereof under precise conditions by virtue of the fact that it renders it possible to dispense exactly determined quantities of the said compositions.

In accordance with the invention, since alkali metal borohydrides are generally intended to be treated by a wet method, that is to say, in aqueous solution or in an appropriate solvent, there are employed as dispersion agents inert products soluble in water or in the aforesaid appropriate solvent. In addition, it is desirable that the said dispersion agents have a relatively low melting point while being solid or pulpy at the storage temperature of the composition containing the borohydrides dispersed in these agents.

The appearance of the mixture obtained depends upon the quantity of the borohydride incorporated and upon the hardness of the wax employed in the preparation of this mixture. Mixtures can be prepared in accordance with the intended use by varying these factors.

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The dispersion agents suitable for carrying the invention into effect include synthetic or natural waxes, products resulting from the polycondensation of ethylene oxide or from a condensation of ethylene oxide with other substances having hydrophilic functions or partially sulphated fatty alcohols.

Products known under the trade name "Carbowax" are entirely suitable as dispersion and coating agents.

The alkali metal borohydrides coated and uniformly dispersed in accordance with the invention in a medium chemically neutral with respect to the said compounds have inter alia the following advantages:

(1) They can be satisfactorily preserved by simple storage in bottles closed by a screw stopper or in other hermetically sealed receptacles.

(2) It is possible safely to mix intimately with the dispersion, catalysts which accelerate the decomposition of the borohydrides or inhibitors retarding this decomposition.

(3) It is possible to prepare compositions having the necessary borohydride content, which may be as low as desired, whereby the laboratory work and the control of operations on an industrial scale are facilitated.

The coating agents are chosen with due regard to the purpose for which the composition containing alkali metal borohydride is to be employed. If, for example, a "Carbowax" is chosen as dispersion and coating agent, preliminary tests will be made and the molecular weight of the "Carbowax" employed will depend upon whether it is desired to utilize the surface-tension, solubilizing or dispersing properties of these waxes when reacting the borohydrides in the presence of water or a suitable solvent.

The following examples are given to enable the manner in which the invention can be carried into effect to be readily understood, but are not to be regarded as limiting the various compositions which can be obtained thereby.

EXAMPLE I

25 grams of the product known under the trade name "Carbowax 1540" (a solid polyethylene glycol) are melted over a water bath, care being taken that the temperature does not exceed 60° C.

15 grams of powdered sodium borohydride are then added with agitation. The mixture is slowly agitated to ensure homogeneity of the mixture until it sets.

A composition according to the invention is thus obtained, which contains 37.5% of sodium borohydride. When kept away from the air, this composition may be used at the desired instant without special precautions.

EXAMPLE II

25 grams of the product known as "Cyclo" wax (fatty alcohol of high molecular weight, partially sulphated) are melted over a water bath, care being taken that the temperature does not exceed 60° C.

25 grams of powdered sodium borohydride are then added with agitation. The mixture is slowly agitated to ensure homogeneity, until it sets.

A composition containing 50% of borohydride is obtained, which remains in a condition of good preservation when kept away from the air and which can be used without special precautions when required.

EXAMPLE III

25 grams of a wax known as "Lanette AO," which is a mixture of polyoxyethylenated normal primary fatty alcohols, are melted under the same conditions as in Examples I and II.

5 grams of sodium borohydride are added with slow agitation, and the mixture is allowed to set. A composition is obtained, which has the same properties of

preservation as those mentioned in the foregoing, and which contains about 16.7% of borohydride.

In all the aforesaid examples, the sodium borohydride may be replaced wholly or in part by potassium borohydride without modifying the method of preparation. It is to be understood that it is possible in accordance with the invention to use other dispersion agents suitable for the same purpose as that performed by the dispersion agents mentioned in the examples.

The above compositions may be used as a reducing agent usually when mixed with water, for any purpose where a reducing agent is required, and finds extensive use in the treatment of hair.

The present invention is based on the direct use of nascent hydrogen for reduction of cystine linkages when it is so used in the treatment of hair. For this purpose a hydrogen-generating product must be used of which the rate of decomposition can be kept under control, and the residual products of which do not damage the hair and can be readily washed out. It has been discovered that solutions of alkaline borohydrides of the type described hereinafter meet these desiderata.

According to the present invention a process for the setting of hair in a desired configuration comprises applying to the hair a freshly prepared aqueous solution of an alkaline borohydride to soften the hair, shaping the hair into the desired configuration, and allowing or causing at least a partial setting of the hair to take place while the hair is so shaped. The invention further includes compositions for use in said process.

By the term alkaline borohydride is meant a borohydride which gives an alkaline reaction in aqueous solution. Suitable borohydrides are, for example, ammonium, sodium, potassium, and lithium borohydrides and substituted borohydrides such as ammonium tetramethoxyborohydride.

The borohydrides thus protected may be employed as starting materials for the preparation of cold or hot waving solutions, giving on the hair results comparable to those usually obtained by conventional methods.

The use of borohydrides affords important advantages. In liberating hydrogen, these products yield the corresponding metaborates (e.g. sodium metaborate, potassium metaborate, lithium metaborate), which products are very well tolerated by the epidermis. The treating solutions prepared from these compounds are not, therefore, attended by the disadvantages of organic mercaptans or inorganic sulphites.

Solutions of borohydrides are reducing agents by virtue of the nascent hydrogen which they evolve. The action of the nascent hydrogen is of very short duration and consequently the hair does not remain impregnated with a reducing solution for so long as in the case of mercaptans or sulphites. The reconstitution of the cystine linkages is simple and rapid. The use of an oxidizing solution is optional. In some cases, simple acid rinsing to eliminate the residual alkalinity of the solution may be sufficient, the reconstitution of the cystine linkages being effected by the oxygen of the air, i.e., an oxidizing rinse need not be employed.

The pH value of aqueous solutions of the foregoing borohydrides is rather high, e.g. above 11. Surprisingly enough, when borohydride solutions are brought into contact with the hair, the pH value of said solutions is gradually lowered and hydrogen commences to form by itself. Very slow at first, the production rate of hydrogen will increase steadily. The decrease of the pH value is probably due to a splitting of the cystine linkages and to the concomitant formation of free —SH groups of an acid character, thus lowering the pH value of the solution in contact with the hair and consequently accelerating the decomposition of the borohydride in solution. Accordingly, the borohydride solutions spontaneously and gradually liberate hydrogen when they are in the presence

of the hair, and two main embodiments of the invention are therefore contemplated:

(a) Adding a buffer to the solution to prevent progressive lowering of the pH value together with a too rapid evolution of hydrogen, and

(b) Using a solution of borohydrides which is not buffered but which is initially stable, i.e., having a pH value in the range 11 to 12.

In the latter case, the decomposition of the borohydride and the evolution of hydrogen can only take place inasmuch as the reducing liquid penetrates into the hair and accordingly the composition employed should comprise auxiliary products to assist it in swelling and penetrating the hair.

When borohydrides, such as sodium borohydride, are employed for the preparation of the solutions intended for cold or hot permanent waving, the pH value of these solutions may, as a rule, be comprised between 7 and 12. The most suitable value for the pH depends upon the nature of the borohydride employed and upon its concentration. The pH value will be chosen, as stated above, in relation to the desired rate of evolution of hydrogen. This rate may also vary in accordance with the temperature at which the permanent waving is carried out.

The action of reducing agents either organic or inorganic, on the cystine linkages is favored by the presence of swelling agents or agents assisting penetration into the hair, such as primary alcohols, urea or its derivatives, thiourea and glycols (ethylene glycol, monobutyl ether and polyglycols). These additives by facilitating the penetration, reduce the time of application of the reducing agent.

Accordingly it is preferred that the hair treating composition should comprise:

(1) An alkaline borohydride or a mixture of borohydrides, preferably coated with or dispersed in water-soluble or emulsifiable inert constituents.

(2) An auxiliary agent regulating the action of the nascent hydrogen on the hair, which agent may be: (a) a buffering agent controlling the pH of the solution to a predetermined value and consequently regulating the rate of decomposition of the alkaline borohydrides; (b) a swelling agent or an agent facilitating penetration into the hair, such as:

Urea, thiourea or formamide,

A primary alcohol or a glycol (e.g. a glycol ether or a polyglycol).

In practice, the composition according to the invention may be presented either as two separate parts, i.e., a powder and/or a paste on the one hand, and a solution on the other hand, which it is sufficient to mix before use, or in the form of a single powder or paste which it is sufficient to dissolve in water.

Composition in two separate parts

FIRST EMBODIMENT

The borohydrides employed are coated and protected as described in Examples I to III, inclusive, and packaged in the form of powder or paste, suitably in a quantity sufficient for one application.

This must be mixed with an aqueous solution, which may comprise either:

(a) A buffer for adjusting the pH value of the final mixture to a suitable value, such as a combination of one or more, of the following compounds: sodium borate, sodium carbonate, hydrogen sodium carbonate, mono-hydrogen ammonium orthophosphate, or mono-hydrogen potassium orthophosphate, etc.

(b) Agents effecting the swelling and/or penetration of the hair.

The concentrations of the hair swelling agents, such as urea or thiourea, may be in the range 10% to 15%.

The concentration of the penetration agents, such as primary alcohols may be from 10% to 45%.

SECOND EMBODIMENT

A first solid composition comprises alkaline borohydrides dispersed in an inert substance, to which there has been added, in the form of powdered products, one or more auxiliary agents controlling the action of nascent hydrogen, for example sodium borate, urea or thiourea.

A second liquid composition, which contains only swelling or penetration products, in liquid form, in solution in water to give a volume of, for example, 100 cc., which is a suitable volume for a good permanent waving.

Composition in the form of a single powder

This powder is composed of all the essential ingredients (except water) in solid form: alkaline borohydrides dispersed in inert constituents, buffering compounds, and swelling or penetrating agents, the latter products being solid or crystalline substances.

In the latter case, it is sufficient to dissolve a powder dose in 100 cc. of water to obtain a cold-waving or hot-waving solution ready for use.

The concentration of alkaline borohydride depends upon the temperature at which the operation is carried out. Generally speaking, concentrations in the range 2% to 6% by weight of the solution ready for use are satisfactory.

The following examples will serve to illustrate the invention but are not to be regarded as limiting it in any way:

EXAMPLE IV

Cold wave

Dispersion of sodium borohydride in Carbowax 1540 in the weight ratio 1:1	gr--	6
Water to make 100 ml.		
pH value		10.3

The dispersion of borohydride in Carbowax is dissolved in the water and the solution thus obtained may be directly applied to the hair to obtain a permanent wave. However, the result obtained is less satisfactory than with compositions according to the following examples, which contain an agent for controlling the rate of evolution of the active hydrogen.

EXAMPLE V

Dispersion of sodium borohydride in Carbowax 1540 in the ratio 1:1 by weight	gr--	6
20% ammonia solution: quantity sufficient to obtain pH 12.		
Water to make 100 ml.		

EXAMPLE VI

Dispersion of sodium borohydride in Carbowax 1540 in the ratio 1:1 by weight	gr--	5
Ethyl alcohol (90%)	gr--	15
Water to make 100 ml.		
pH value		10.3

EXAMPLE VII

Dispersion of sodium borohydride in Carbowax 1540 in the ratio 1:1 by weight	gr--	6
Urea	gr--	10
Water to make 100 ml.		
pH value		10.2

EXAMPLE VIII

Dispersion of sodium borohydride in Carabowax 1540 in the ratio 1:1 by weight	gr--	6
Ethyl alcohol (90%)	gr--	15
Urea	gr--	10
Water to make 100 ml.		
pH value		10.2

EXAMPLE IX

Dispersion of sodium borohydride in Carbowax 1540 in the ratio 1:1 by weight	gr--	8
Sodium borate	gr--	0.5
Ethyl alcohol	gr--	4
Thiourea	gr--	7
Water to make 100 ml.		
pH value		9.3

EXAMPLE X

Sodium borohydride	Gr.	3
Glycocoll		2
Urea		6
Carbowax 1540		11

EXAMPLE XI

Sodium borohydride		3
Glycocoll		1
Lactamide		4
Carbowax 1500		10

EXAMPLE XII

Sodium borohydride		2
Glycocoll		1
Thiourea		12
Carbowax 1500		5
Polyethyleneglycol 1300		5

EXAMPLE XIII

Sodium borohydride		2
Boric oxide B ₂ O ₃		2
Carbowax 4000		6

EXAMPLE XIV

Sodium borohydride		3
Glycocoll		2
Carbowax 6000		4
Polyethyleneglycol 1300		2

EXAMPLE XV

Sodium borohydride		4
Boric oxide B ₂ O ₃		2
Methoxyacetamide		4
Carbowax 1540		10

EXAMPLE XVI

Glycocoll		1
Potassium borohydride		3
Glycolamide		6
Carbowax 4000		8

EXAMPLE XVII

Potassium borohydride		1.5
Alanine (alpha aminopropionic acid)		2
Glycolamide		7
Carbowax 1500		8

EXAMPLE XVIII

Sodium borohydride		3
Glycocoll		1
"Lanette AO" wax		6

EXAMPLE XIX

Potassium borohydride		2.5
Glycocoll		2
"Lanette AO" wax		5

EXAMPLE XX

Sodium borohydride		2
Boric oxide B ₂ O ₃		2
Acetamide		4
"Lanette AO" wax		4
Carbowax 1540		3

EXAMPLE XXI

Sodium borohydride	3
Alanine (alpha aminopropionic acid)	2
Isobutylamide	6
"Lanette AO" wax	10

EXAMPLE XXII

Sodium borohydride	3
Boric acid B ₂ O ₃	0.5
Thiourea	8
"Sipol AO" wax	12

EXAMPLE XXIII

Sodium borohydride	2
Glycocoll	1
Malonamide	5
"Cyclo" wax	4

EXAMPLE XXIV

Potassium borohydride	1
Glycocoll	0.5
Cyanacetamide	3
"Lanette SX" wax	3

EXAMPLE XXV

Sodium borohydride	1.5
Potassium borohydride	1.5
Glycocoll	1.5
Urea	5
"Sipol AO" wax	5
"Lanette SX" wax	5

EXAMPLE XXVI

Sodium borohydride	2
Boric acid B ₂ O ₃	0.5
Alanine	1
"Cyclo" wax	3
Carbowax 1500	3

EXAMPLE XXVII

Potassium borohydride	5
Glycocoll	2
Acetamide	7
"Cyclo" wax	6
"Sipol AO" wax	6

EXAMPLE XXVIII

Sodium borohydride	3
Potassium borohydride	1
Glycocoll	0.5
Urea	6
Lactamide	6
"Sipol AO" wax	6
Carbowax 4000	4

EXAMPLE XXIX

Sodium borohydride	3.5
Alanine	1
Thiourea	3
Methoxyacetamide	3
Carbowax 1540	2.5
"Lanette AO" wax	2.5
"Cyclo" wax	2.5

In Examples V to IX the mixture of borohydride and Carbowax is added to the solution of the other ingredients at the time of use.

On human hair a solution as above is employed in the following manner:

The hair is moistened with the solution. It is then wound on curlers of such size as to distribute about 60 of them over the whole head of hair. The winding must be effected normally and must be neither too loose nor too tight. The hair wound on the curlers is saturated with the reducing liquid. The setting time for all the curlers is about 25 to 30 minutes and the hair is rinsed

with water before being unwound from the curlers. The hair is then rinsed with a solution of an organic acid, e.g. lactic acid, citric acid, or tartaric acid, in a concentration of e.g. 1 part per thousand, the object of this rinsing being to eliminate the residual alkalinity from the reducing solution.

An excellent "permanent" wave is thus obtained, the hair remaining very flexible.

EXAMPLE XXX

50% potassium borohydride dispersion in "Lanette Wax AO" (trade name of a polyoxyalkylene derivative of higher aliphatic alcohols)	10
Buffer:	
(Anhydrous sodium carbonate)	0.5
(Hydrogen sodium carbonate)	0.45
Water to make 100 ml.	
pH value	10.2

The method of impregnating the hair and the time of reduction correspond to the particulars given in Example IX.

The hair is then rinsed with water, and then with an oxidizing rinse consisting of 80 to 100 ml. of a 1.2 percent hydrogen peroxide solution instead of the final rinse.

Machine wave

The setting time may be reduced, e.g. the reducing liquid prepared as in the foregoing examples may be allowed to act for only 15 instead of 30 minutes, by employing a heating hood of a type commonly used in hairdressing saloons. The heat or steam produces a temperature increase over the whole of the hair wound on the curlers, up to about 45° C. A faster penetration and decomposition of the reducing solution will follow, thus enabling a shorter time during which the reaction is allowed to proceed. The solutions employed at this temperature are the same as those referred to in the foregoing examples for the cold wave.

Thermal wave

Reducing solutions of the type referred to in Examples IV to X may be used to carry out hot waving in the following manner.

EXAMPLE XXXI

A solution is prepared containing:

50% sodium borohydride dispersion in "Carbowax 1540" (trade name of a polyethyleneglycol of a molecular weight higher than 1,000)	8
Buffer:	
(Monohydrogen sodium phosphate)	0.72
(Solid caustic soda)	0.2
Thiourea	7
Ethyl alcohol	5
Water to make 100 ml.	
pH value	11.5

The bulk of hair is divided into 32 tresses, which are wound on curlers. There are disposed on these curled tresses heaters capable of maintaining a temperature of about 100° C. for 2 to 5 minutes. The heaters are then removed and all the tresses are allowed to cool.

The tresses are unwound and the hair is rinsed with a 1% lactic acid solution. A flexible, strong wave is obtained.

Decurling.—The splitting of the cystine linkages produced by the nascent hydrogen resulting from the decomposition of the borohydrides produces, as is known, a temporary plasticization of the hair which permits not only curling but also decurling.

It is therefore possible with compositions suitably compounded within the limits hereinbefore set forth, to decurl hair which is excessively curled either naturally

(crisp hair), or artificially by a previous wave (crimped hair).

The following procedure is adopted:

EXAMPLE XXXII

A solution is prepared containing:

50% potassium borohydride suspension in "Lanette Wax SX" (trade name of a mixture of free and sulphated higher aliphatic alcohols) -----gr--	4
Buffer:	
(Boric acid) -----gr--	0.36
(Solid caustic soda) -----gr--	0.16
Ethyl alcohol -----gr--	4
Urea -----gr--	12
Water to make 100 ml.	
pH value -----	9.3

The whole hair is moistened by the above solution and allowed to stand for 5 minutes. The hair is combed so as to stretch it out and then rinsed first with water and then with an acid rinse, e.g. 1 part per thousand of citric acid, to eliminate the alkalinity of the spent liquor.

A relaxation of the permanent wave or of the natural crimp of the order of 40% may thus be obtained.

In the above composition the buffering agent and the swelling agent may be incorporated in the coating material.

This application is a continuation-in-part of application Serial No. 573,618, filed March 26, 1956 (now abandoned), which depends for priority on French application Serial No. 688,761, filed in France March 31, 1955, and U.S. application Serial No. 593,364, filed June 25, 1956 (now abandoned), which claims the priority of French application Serial No. 694,836, filed in France June 29, 1955.

I claim:

1. An anhydrous stable alkali metal borohydride composition containing at least one alkali metal borohydride dispersed in a water soluble wax-like coating and protecting agent selected from the group consisting of a solid polyethyleneglycol, a waxy partially sulphated high molecular weight fatty alcohol and a mixture of polyoxyethylenated normal primary fatty alcohols.

2. An anhydrous stable alkali metal borohydride composition containing at least one alkali metal borohydride dispersed in a water-soluble wax-like coating and protecting agent consisting of a solid polyethyleneglycol.

3. An anhydrous stable alkali metal borohydride composition containing at least one alkali metal borohydride dispersed in a water-soluble wax-like coating and protecting agent consisting of partially sulphated high molecular weight fatty alcohol.

4. An anhydrous stable alkali metal borohydride composition containing at least one alkali metal borohydride dispersed in a water soluble wax-like coating and protecting agent consisting of a mixture of polyoxyethylenated normal primary fatty alcohols.

5. An anhydrous stable alkali metal borohydride composition containing at least one alkali metal borohydride and a pH buffering agent dispersed in a water soluble wax-like coating and protecting agent selected from the group consisting of a solid polyethylene glycol, a waxy partially sulphated high molecular weight fatty alcohol and a mixture of polyoxyethylenated normal primary fatty alcohols.

6. An anhydrous stable alkali metal borohydride composition containing at least one alkali metal borohydride and a hair swelling agent dispersed in a water soluble wax-like coating and protecting agent selected from the group consisting of a solid polyethylene glycol, a waxy partially sulphated high molecular weight fatty alcohol and a mixture of polyoxyethylenated normal primary fatty alcohols.

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