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3,801,709

FRAGRANCE RETENTION BY CHELATING AGENT COATED TALC

Larry Louis Augsburg, Baltimore, Md., and John Ray
Marvel, East Brunswick, N.J., assignors to Johnson &
Johnson, New Brunswick, N.J.

No Drawing. Filed Oct. 27, 1970, Ser. No. 84,519

Int. Cl. A61k 7/02; A61e 13/00; C11b 9/00

U.S. Cl. 424-69

7 Claims

ABSTRACT OF THE DISCLOSURE

Compositions comprising finely divided materials having fragrance ingredients, i.e. perfume associated therewith are improved in the ability to retain such fragrances without deteriorating over a period of time by treating said materials with a chelating substance. It is postulated that various components of the finely divided materials that would otherwise react with said perfume and degrade it are inactivated. Both the process of inactivation and the compositions resulting therefrom embody the inventive concept.

CROSS REFERENCES TO RELATED APPLICATIONS

There are no related applications by this inventorship entity.

BRIEF SUMMARY OF THE INVENTION

Finely divided active materials having fragrance ingredients are treated with small quantities of a chelating material. It is theorized that the active impurity metallic ions contained in the finely divided material are inactivated by the chelant and therefore the fragrance material is protected from the degradative action of said metal ions.

BACKGROUND OF THE INVENTION

Various body powders, particularly talc products have been used for many years on the skin in the form of finely divided powder. Conventionally, talc is ground to a fine state using grinding media such as ball mills, roller mills, jet mills and the like to produce finely-divided talcs over a wide range of mesh sizes.

Very frequently, for many uses of the finely divided talc, it is necessary to add various quantities, usually in minor proportions, of fragrance materials, i.e. perfume, to mask the natural odor of the talc or to impart an entirely new fragrance to it.

It is well known that perfumes are extremely delicate and fleeting. Again, it is common knowledge that some odors that are unpleasant in high concentration are distinctly agreeable when dilute. Certain definite concentrations of perfumes are therefore necessary in products for their pleasant effect on the olfactory senses. In products intended for long shelf life it is important that the perfume concentration and component ratio remain essentially the same character on aging, so that the aroma of freshly prepared product is just as pleasant as that of aged product. In sensing the aroma of a particular perfumed product, a certain volatilization is necessary since a minute amount of the aroma has to reach the olfactory senses.

In certain perfumed powder substrate, such as talcs,

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however, chemical changes, such as oxidation, also take place due to the effect of certain metal ions, such as, for example, iron and nickel which occur as contaminants in natural talc ore. These chemical changes in the perfume result in rapid loss of effectiveness, generating an "off odor," and in general giving an unsatisfactory odor due to the reaction products formed.

Some grades of talc are essentially free of reactive ions. These do not present a serious problem in fragrance degradation. Therefore, the major thrust of the invention is for talcs that contain active metal ions that cannot easily be removed.

Perfumes used in combination with talc usually have as their essential components both natural and synthetic ingredients. The overall fragrance on talc will undergo alterations with aging due either to volatilization of components, i.e. fractionation, and/or chemical changes, i.e. oxidation, esterification, etc.

Certain of the chemical changes are accelerated, probably catalytically, by the presence of certain trace metallic ions, such as iron or nickel. These ions are tightly bound in the crystal lattice of the talc as contaminants and cannot economically be removed by normal purification techniques.

Attempts to improve fragrance retention in talc compositions have been numerous, but none of them have solved the problem in a practical manner.

DETAILED DESCRIPTION OF THE INVENTION

It has now been discovered and forms the major feature of this invention that when chelating agents are added to powdered substrates in an aqueous environment and said treated substrates are dried in situ, long-term fragrance stabilization is accomplished.

Thus, it is an advantage of this invention that finely, divided, solid, materials such as talc can be suitably treated with an aqueous medium, containing small quantities of a chelating agent, in order to prevent the active components in the solid materials from causing degradation of odor imparting materials.

In general, the aqueous solution of chelating agent is applied to the finely divided solid materials by wetting the divided materials in any convenient conventional manner, such as by forming a slurry of the solid materials in a solution containing chelating agent, filtering and drying the resultant filter cake. It is also possible to apply the chelating agent by any other means resulting in the wetting of the powder, i.e. spraying the powder in a fluid bed process with a solution containing small amounts of chelating agent.

The resulting finely divided material, i.e. talc will usually contain from 0.05 to 3, preferably .1 to 2 and most preferably .1 to 1 weight percent chelating agent dispersed on the outer surfaces of each particle.

It is important that the chelating agent be dried on the product since this step apparently provides a means to deactivate the active metal sites in the crystal lattice. This eliminates the possibility of their reaction with the perfume.

The chemical bond formed between chelating agents and the metal is strong enough to withstand further treatments which are necessary in preparing special commer-

cial products, such as, for example, perfumed medicated powder, cosmetic, face, and other powder products.

The chelating treatment works well on both types of talc products conventionally termed platy and nonplaty.

In order to attain the very thin but effective coating of chelating agent on the finely divided particles the chelating agent should be added as an aqueous solution. The concentration in the solution must be a value low enough to give the desired distribution by providing sufficient water and high enough concentration to give the desired amount of chelating agent when the water is removed by drying. This choice of concentration depends on several factors such as solubility of the chelating agent, the particle size of the talc, the drying capacity of the equipment, etc. Generally, there will be from 0.01 to 50 wt. percent of the chelating agent in the solvent.

It is economically advantageous to include the chelating treatment into the normal process of talc beneficiation such that the chelating step is inserted between the final drying step and a final floatation step. In that case, however, the amount of moisture present in the wet, undried talc must be accounted for in making up the solution containing the chelating agent.

The finely divided materials which can be treated by the process of the invention include those materials of a mesh size conventionally associated with body powders and other powdered materials in the range of 0.1 to 200 microns.

Since these materials are to be treated with aqueous materials, they are generally insoluble in water. Such materials include body powders such as talc, various adsorbents such as molecular sieves, abrasives, and the like.

The class of materials considered as chelating agents is large but all can be considered as within the genus of this invention as well as other type agents such as clathrate compounds which interact with certain metal ions to neutralize them in terms of those ion's ability to catalyze perfume agents.

Examples of suitable chelating agents include, ethylenediaminetetraacetic acid tetrasodium salt, N-hydroxyethylethylenediaminetriacetic acid trisodium salt, nitrilotriacetic acid trisodium salt, the corresponding potassium, calcium magnesium and lithium salts of these three compounds and mixed alkali metal salts thereof, alkali metal salts of the sugar acids such as lactic, citric, gluconic, and 2-ketogluconic as well as other aldonic and dibasic acids produced from sugars by chemical oxidation. Specific sugar acid salts include sodium lactate, sodium citrate, potassium sodium tartrate, sodium arabonate, sodium gluconate, sodium galactonate, potassium sodium saccharate, sodium mucate, sodium glucoheptonate.

For the purposes of this application, the term "chelation" is taken to mean the ability of a compound to remove or associate with polyvalent metal ions such as Fe^{+++} by forming complex ring structures. Sometimes the term sequestration is used interchangeably with chelation, but in actuality sequestration is understood for the purposes of this application to mean the ability of a substance to entrap polyvalent metal ions and keep them in solution.

Other suitable chelating agents that are widely available include those materials that are used in detergent formulations as builders. These include such materials as sodium polyphosphates, borates, condensed polyphosphates, nitrilotriacetates and the like.

Particularly preferred chelating agents for the purposes of the invention are:

ethylenediaminetetraacetate, disodium salt;
ethylenediaminetetraacetate, tetrasodium salt;
N,N-dihydroxyethylglycine, sodium salt;
hydroxyethylethylenediaminetriacetate, trisodium salt;
sodium glucoheptonate;
ethylenediaminetetraacetate, calciumdisodium salt;
nitrilotriacetate, trisodium salt;

Chelating agents are described in full in the art in articles such as those appearing in Chem Week, 70, #3, 39 (1952), and Ind. Eng. Chem., 45 338 (1953).

Talc, in its broadest definition includes rock which grades from essentially pure mineral talc to talcose rocks which contain less than 50% mineral talc mixed with carbonates, amphiboles and serpentine. Talc, the mineral, is a hydrous magnesium silicate. The higher grade talcs usually are associated with metamorphosed sediments, such as dolomite, marble, and magnesite. The usual contaminants in high-grade talc are carbonates and tremolite, and sometimes chlorite, pyroxane, sulfides, sericite, rutile, zircon, quartz, pyrite, and iron oxides. All impurities are objectionable to some degree and efforts are described in the prior art to eliminate these impurities from talc. However, even with the best technique trace amounts of metals are present in the crystal lattice of certain talcs and they act as catalysts in the degradation of perfume in finished products.

The compositions of matter of the invention comprise finely divided material treated as described above and which contain the chelating agent adsorbed on their external surfaces.

Commercial perfumes are mixtures of many components. These components all contribute to the particular fragrance which is characteristic of the mixture. For obtaining the desired fragrance, the ratio of components might be changed, some components may be added and some omitted.

The unpleasant odor, (sometimes described as "chalky") is observed after interaction of some of the perfume components with the talc substrate containing free metals or metals in the crystal lattice. It is virtually impossible, however, to identify the components which produce this undesired odor since the process of elimination is almost infinite.

Also, to test the components individually on a powder substrate would be meaningless since the change of aroma of one component would not necessarily signify a contribution to the "chalky" or undesired odor of the perfume on a talc substrate. Therefore, the only possible approach to the problem at the present time, considering the state of the art, is to determine the odor of the total perfume mixture after fixed periods of time.

Examples of typical perfume components which can be formulated to make up a particular pleasant aroma when used in a body powder product include: lemon oil, musk Ketone, ionone, diphenyl oxide, cedarwood-terpeneless; Aldehyde C-12; geranyl acetate; ylang ylang oil; cedryl acetate, isoeugenol; cinnamic alcohol, aurantheol, methyl anthranilate; vanillin, oil bergamot, eugenol; oil of cananga; citral; tetrahydro linalool; oil patchouly, methyl isoeugenol; hexylcinnamic aldehyde; resin oilbanum, resin balsam fir; musk aurbrette, resin balsam Peru; oil sandalwood, geraniol; terpenyl acetate, benzyl isoeugenol; oil copaiba; oil nutmegs; rhodinol; diphenyl methane; hydroxycitronellal; methyl benzoate; benzyl propionate; oil palmarose; oil orange, oil geranium; methyl gamma ionone; oil of lavender.

In testing for the effects of perfumes in a certain product an organoleptic or sensory evaluation is employed since analytical or instrumental methods are generally not capable of accomplishing this satisfactorily.

Although certain correlations can be made between sensory and instrumental results, acceptability of a product for consumer use ultimately depends on sensory evaluation. Testing in the examples of this invention was accomplished by the use of sensory panels consisting of judges selected for sensory acuity and then trained to recognize, identify and discriminate subtle differences in the particular sensory characteristics being evaluated. The combined judgments of the sensory panel thus represent a kind of consensus aimed at averaging individual variations. When due recognition is given to the limitations

of this kind of subjective testing, meaningful and useful results can be obtained by sensory panel methods.

Evaluations were carried out in accordance with The American Society for Testing and Material (ASTM) STP 434 method described in the Manual on Sensory Testing Methods. Testing in accordance with this procedure is referred to herein as "organoleptic testing."

The preferred solvent for the chelating agents is water, of course, since it is the least expensive among the solvents which could be used and also for ease of incorporation of the chelating step into the procedure in treating the "wet," undried talc obtained after the final floatation. Other solvents, however, might also be used, such as, for example, alcohols. The only requisite in using a solvent of choice is that the same be able to dissolve the necessary amount of chelating agent.

The invention will be further understood by reference to the following examples. (All percentages in this application are weight percentages unless otherwise indicated.)

EXAMPLE 1

A finely-divided talc containing approximately 2.5% iron was acid treated in order to extract metals present therein: a solution of 236 ml. of concentrated HCl was mixed with 764 ml. of distilled water and added to 500 gm. of said talc. After about 15 minutes of mixing, the resultant slurry was kept at 50° C. for one hour and a half on a steam bath.

The slurry was filtered and washed under vacuum until neutral. Approximately 700 ml. of the first filtrate was saved for further analysis. The filtered talc was dried at 90° C. in a forced draft oven for 21.5 hours.

Analytical tests run on the filtrate showed the following concentrations of metals in milligram/ml. of solution: Fe 0.462, Ni 0.048, Cu 0.00061.

The resultant talc was washed free of acid, dried, and 0.2% by weight of perfume was added. The resultant powder was thoroughly mixed in a V blender.

Organoleptic evaluation indicated the same possessed a very "chalky" odor after ageing for 4 weeks at 120° F. Thus, it is plain that extraction with acid to remove metal was not successful indicating some metal ions are very tightly bound. Analysis showed a considerable amount of metal remained in the talc.

EXAMPLE 2

A portion of the untreated talc of Example 1 was treated with a warm aqueous solution of EDTA (ethylenediaminetetraacetate, tetrasodium salt) as follows:

40 gm. of EDTA was mixed with 400 mls. of distilled water. The mixture was stirred with a stirring rod until the EDTA had dissolved. The solution was added to the talc, which was then slurried to a paste. The resultant slurry was heated to 180° F. and held there for an hour, after which it was filtered through a Buchner filter funnel and the original liquid was saved for metal analysis.

The remaining talc in the filter funnel was then washed thoroughly with distilled water and dried at 70° C. The first filtrate which was analyzed contained 0.318 mg./ml. of Fe and 0.0033 milligram/ml. of Ni.

0.2% perfume was added to the dried powder.

By organoleptic testing methods, the sample had a chalky odor after ageing according to 75% of the panel members.

From the above samples it is seen that the metals in the talc are tenaciously held in the crystal lattice and cannot be washed out with acids and therefore improved talc products insofar as fragrance stability is concerned cannot be made with these chemically obvious treatments.

EXAMPLE 3

A series of five samples were prepared from the untreated talc (which contained approximately 2.5% total naturally present iron and nickel) of Example 1.

(A) Untreated talc.

(B) 0.5% Na₂ EDTA was added dry to talc of A.

(C) 1.0% Na₂ EDTA was added dry to talc of A.

(D) 0.5% Na₄ EDTA was added dry to talc of A.

(E) 1.0% of Na₄ EDTA was added dry to talc of A.

Each sample was mixed with 0.2% perfume and aged at 120° F. Organoleptic evaluation of the samples showed the following results given as percent of panel members sensing the characteristic undesired "chalky" odor.¹

Dry addition of the chelating agents leaves the particle surfaces of talc intact causing no change in activities of the metal present thereon.

However, when talc samples are treated with chelating agent according to the invention, the resultant powders are quite satisfactory. In each of the examples F through I, the specified chelating agent is added at the indicated percentage by the following procedure:

A solution containing the calculated amount of chelate to be deposited on 5000 grams of talc is dissolved in 250 mls. of water. The solution was sprayed onto the talc with mixing so that the solution uniformly coats the talc. The wet mixture was dried overnight in an oven at 60° C.

(F) 0.5% of Na₄ EDTA is coated onto 99.3% of talc according to the procedure above, then 0.2% of perfume was mixed therewith. The sample was aged at 120° F. for 4, 8 and 12 weeks and subjected to organoleptic evaluation which showed respectively 5, 30 and 5 percent of response for "chalkiness."

(G) 1.0% of Na₄ EDTA was coated onto 98.8% of talc according to the procedure above, then 0.2% of perfume was mixed therewith. The sample was aged at 120° F. for 4, 8 and 12 weeks and subjected to organoleptic evaluation. The results respectively were 20, 25 and 10 percent response for "chalkiness".

(H) 0.5% of Na₂ EDTA was coated onto 99.3% of talc according to the procedure above, then 0.2% of perfume was mixed therewith. The sample was aged at 120° F. for 4, 8 and 12 weeks and subjected to organoleptic evaluation. The response for "chalkiness" were 30, 35 and 35 respectively.

(I) 1.0% Na₂ EDTA was coated onto 98.8% of talc according to the procedure above, then 0.2% of perfume was mixed therewith. The sample was aged at 120° F. for 4, 8 and 12 weeks and subjected to organoleptic evaluation. Results were respectively 30, 35 and 15% "chalkiness". The results obtained from Samples A-i are summarized below in Table I. The use of chelants decreases the chalkiness odor.²

TABLE I

	4 weeks	8 weeks	12 weeks	Average response
Sample:				
A (control)-----	60	45	60	55
B-----	45	60	60	55
C-----	45	55	35	45
D-----	75	80	85	80
E-----	85	95	75	85
F-----	5	30	5	13
G-----	20	25	10	18
H-----	30	35	35	33
I-----	30	35	15	27

EXAMPLE 4

Each talc sample contained approximately 2.5% of active metal ions, primarily iron and nickel. All samples contained the same perfume at the same concentration. After perfume addition, all samples were evaluated organoleptically together with appropriate standards. The results are summarized below in Table II (percent of panel members sensing the undesired chalky odor).

¹The organoleptic results are summarized hereafter in Table I.

²All samples in the examples of this application exhibit virtually no chalkiness odor initially, before aging.

The chelating agents are added in aqueous solution as described in Example 3.

TABLE II

4. The method of claim 1 in which said chelating agent is hydroxyethylenediaminetriacetic acid or its salt.

Form number	Treatment, percent Na ₄ EDTA	Percent response for chalkiness at 120° F. after—			Average response
		4 weeks	8 weeks	12 weeks	
J (control).....	+None	55	45	60	53
K (control).....	+0.5	20	35	15	23
L (control).....	+0.3	35	5	15	18
M (control).....	+0.2	15	20	15	17
N (control).....	+0.1	30	55	30	35
O (control).....	+0.05	50	45	45	46
P (control).....	+0.02	50	55	65	56
Na ² EDTA					
Q (control).....	+0.5	15	20	30	22
R (control).....	+0.3	15	10	25	17
S (control).....	+0.2	35	20	40	32
T (control).....	+0.1	20	25	30	25
U (control).....	+0.05	25	25	45	32
V (control).....	+0.02	65	25	60	60
Sodium glucoheptanate					
W (control).....	+0.1	20	25	15	20
X (control).....	+0.25	5	25	25	18
Y (control).....	+0.50	15	15	10	13
CaNa ₂ EDTA					
Z (control).....	+0.25	40	25	30	32
Sodium N,N-dihydroxyethylglycine					
ZZ (control).....	+0.25	0	5	30	12
Trisodium N-hydroxyethyl ethylenediamine-triacetate					
ZY (control).....	+0.25	0	20	15	12

As can be seen by the above data, concentrations of various chelating agents within the prescribed ranges are very effective in reducing the chalkiness response after aging of perfumed talc.

EXAMPLE 5

Odor stability is related to chemical stability. It was found that one paralleled the other. One percent amyl cinnamic aldehyde was placed on untreated talc containing about 2.5% metal impurities. The aldehyde was found to degrade at a rate of 1.7×10^{-3} /hr., while undergoing a distinctly noticeable odor deterioration. In contrast, an identical talc sample containing 0.2 wt. percent of Na₄ EDTA and one percent amyl cinnamic aldehyde was tested with the same analytical techniques. No degradation was detected. The odor was unchanged (organoleptically) over a period of 13 days at 120° F.

What is claimed is:

1. The method of producing an organoleptically stable composition resistant to odor degradation comprising the steps of treating finely divided talcose mineral particles containing in the crystal lattice thereof small quantities of polyvalent metal impurities with a solution containing from 0.01 to 50% by weight of a chelating agent; evaporating the solvent of said solution to thereby fix a residual coating of from .05 to 3% by weight of the composition of the chelating agent on the surface of said mineral particles; and thereafter admixing with the chelated talcose mineral a small but organoleptically effective amount of a perfume agent.

2. The method of claim 1 in which said chelating agent is ethylenediaminetetraacetic acid or its salt.

3. The method of claim 1 in which said chelating agent is N,N-dihydroxyethylglycine or its salt.

5. The method of claim 1 in which said chelating agent is glucoheptonate or its salt.

6. The method of claim 1 in which said chelating agent is nitrilotriacetic acid or its salt.

7. The organoleptically stable composition prepared by the method of claim 1.

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ALBERT T. MEYERS, Primary Examiner

A. P. FAGELSON, Assistant Examiner

U.S. Cl. X.R.

106—306; 252—522; 424—76