J. Soc. Cosmet. Chem., **22**, 153–160 (March 4, 1971)

Physical Behavior of Aluminum Chlorhydroxide Suspensions for Aerosol Formulations

J. M. CROTTY, B.S., R. L. RAYMOND, B.S., and B. SIEGAL, Ph.D.*

Presented May 26–27, 1970, New York City

Synopsis—In light of current theory, this paper describes several factors governing the character of SUSPENSIONS containing ALUMINUM CHLORHYDROXIDE to be dispensed in AEROSOL form for antiperspirant use. In particular, systems employing fumed SILICA as the suspending agent are treated in detail. The effect of moisture content, polarity, and particle size of the substituents upon viscosity and homogeneity are discussed.

INTRODUCTION

The formulation of nonaqueous, nonalcoholic suspensions of aluminum chlorhydroxide for aerosol antiperspirants has presented a unique problem to the formulation chemist. This is due to the difference in physical behavior between the suspension as a concentrate and the suspension as a finished aerosol. The two systems differ in dilution, degree of particle sedimentation, and viscosity.

In the finished aerosol, or dilute system, the life of suspension before soft settling of the particles, the degree of particle agglomeration or caking, and the ease of particle redispersion are critical factors dependent on the concentration of the suspending agent. In the concentrate system, the viscosity of the suspension is the critical factor also dependent on the concentration of the suspending agent.

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* Gillette Co. Toiletries Div., Gillette Park, South Boston, Mass. 02106.

In order to achieve the desirable characteristics in the dilute form, it may be necessary to increase the viscosity of the concentrate beyond the level which will facilitate the manufacturing of the product. It is the purpose of this paper to discuss some physical parameters which affect the viscosity of aluminum chlorhydroxide suspensions as concentrates and their effect on the finished aerosol.

SUSPENSIONS: GENERAL CONSIDERATIONS

A suspension is a system in which insoluble solid particles of a material are dispersed throughout a liquid vehicle. The particles in suspension settle under the force of gravity. This effect is qualitatively expressed by Stokes' law which relates the rate of sedimentation to the difference in densities between the particle and medium, times the square of the particle radius, divided by the viscosity of the vehicle.

$$\text{Rate} = \frac{Kr^2\,(d_p - d_m)}{v}$$

Stokes' law assumes that the particles are spheres of the same size, that there is no interaction between the particle and the medium, and that electrokinetic factors are not involved. This is rarely the case, especially in more concentrated suspensions. The limitations and extensions of Stokes' law have been reviewed elsewhere (1).

Generally, there are two types of suspensions in practice:

1. Colloidally stable or deflocculated suspensions. In this case, electrokinetic factors have been adjusted to allow the forces of repulsion between particles to outweigh the van der Waals forces of energy associating particles. This will prevent the aggregation of the particles. Colloidally stable suspensions have been reviewed by Cartwright (2).
2. Controlled flocculation suspensions. These are usually achieved by the addition of surface active ingredients or suspending agents which cause the particles to settle as loose flocs (open structures) which are redispersed easily.

The system of immediate interest is a controlled flocculation suspension achieved by the addition of fumed or pyrogenic silica as the suspending agent.

The mechanism of fumed silica as a suspending agent is as follows: Each particle has a very large surface area with hydroxyl groups attached to the silicon atoms on the particle surface. When the material is dispersed in a suspension, its particles link together at the hydroxyl sites through hydrogen bonding. The effect produced is a three-dimensional cell-like structure similar to a honeycomb. Each cell traps a portion of the suspension and restricts free movement of fluid and particles (3).

In addition, there is probably a build-up of positive charge by the aluminum chlorhydroxide particles, which is partially neutralized by the negative charge of fumed silica. This overcomes the electrokinetic force of repulsion between particles and allows the flocs to form.

Fumed silica in the concentrate retards sedimentation by increasing viscosity. It produces a system which is pseudoplastic and thixotropic in nature.

EXPERIMENTAL

Materials

Antiperspirant Concentrate

The following typical antiperspirant concentrate was used as a control. When the concentration of any of the ingredients was varied, the difference was made up with isopropyl ester.

Aluminum chlorhydroxide	33.0%
Fumed silica	4.0%
Additives	3.9%
Isopropyl ester	q.s.

About 10% of this concentrate was then diluted with a low pressure fluorocarbon propellant to produce the finished product.

Aluminum Chlorhydroxide

Two commercially available grades of aluminum chlorhydroxide were selected.

(a) Impalpable powder with the following particle size distribution:

Micron size	0–2	2–5	5–10	10–17	17–27	27–34	34
% composition	1.9	4.5	25.3	28.9	31.1	7.5	0.8

This was evaluated at two concentrations (33% and 41% by weight in the suspension).

(b) Ultrafine powder with the following particle size distribution:

Micron size	0–2	2–5	5–10	10–17	17–27	27–34	34
% composition	0.7	8.1	66.2	23.3	1.6	0.1	---

Both particle size distributions are typical for these grades of aluminum chlorhydroxide.

Fumed Silica

A commercially available grade of fumed silica was selected for use. It has a surface area of 200 m^2/g. Evaluations were made at 3.0, 3.5, and 4.0% by weight in the concentrate suspension.

Additives

The following additives to the concentrate suspension were evaluated.

Perfume—A custom perfume was evaluated at 3.5% and 5.0% by weight.

Phenolic Antibacterial—A commercially available grade of hexachlorophene was evaluated at 0.4% and 1.0% by weight.

Quaternary Antibacterial—A commercially available grade of benzethonium chloride was evaluated at 0.5% by weight.

Isopropyl Ester

A commercially available product containing approximately 95% isopropyl myristate and 5% various other isopropyl esters was selected.

Test Procedures

Water Determination

A modified Karl Fischer water determination was performed by adding a 50% excess of Karl Fischer reagent, allowing 10 min for complete reaction, then back-titrating with standard water-in-methanol reagent.

Particle Size Distribution (PSD)

PSD was determined with a Coulter Counter, Model B,* containing a 70-μ aperture (4) and equipped with a volume converter, Model M.*

Viscosity Measurement

After the suspensions were allowed to sit for 2 min after preparation, measurements of apparent viscosity were made using a Brookfield RVT Viscometer,† equipped with a disc spindle No. 3 at 10 rpm. Readings were taken after the fourth revolution.

Preparation of Suspensions

Quantities (300 g) of each suspension were prepared using the following order of addition: isopropyl ester, additives, aluminum chlorhydroxide, fumed silica.

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* Coulter Electronics, Industrial Div., 590 W. 20th St., Hialeah, Fla. 33010.

† Brookfield Engineering Laboratories, Inc., 240 Cushing St., Stoughton, Mass. 02072.

The suspensions were then hand-stirred for 2 min in order to wet the solid components. This was followed by mechanical stirring for 2 min with a Lightnin Mixer* at about 1165 rpm. The suspensions were then allowed to sit for 2 min, after which viscosity measurements were made.

RESULTS AND DISCUSSION

The concentration of fumed silica in the concentrate system has the most dramatic effect on apparent viscosity (hereafter referred to as viscosity) of all variables evaluated. Table I illustrates the marked increase in viscosity produced by small increases in fumed silica content. However, the suspension stability of the finished aerosol formulation is equally dependent on the concentration of fumed silica. This was shown when the concentrate suspensions from Table I which contained different concentrations of fumed silica were diluted to the aerosol form. The sedimentation volumes increased with increasing concentrations of fumed silica. This is the only viscosity-influencing variable in the concentration suspension which correspondingly influences the suspension stability of the finished aerosol.

The threshold level for viscosity between a pourable liquid and a nonpourable cream is approximately 5000 cps. For manufacturing pur-

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*Mixing Equipment Co. Inc., 136 Mt. Blvd., Rochester, N. Y. 14603.

Table I

Effect of Concentration of Ingredients on Viscosity

Ingredient	Concentration (%)		Viscosity (cps)
Fumed silica	3.0		1250
Fumed silica	3.5		1950
Fumed silica	4.0	(Control)	2900
Water	7.0	(Control)	2900
Water	7.5		7850
Water	8.0		8950
Aluminum chlorhydroxide	33.0	(Control)	2900
Aluminum chlorhydroxide	41.0		8500
Hexachlorophene	0		2900
Hexachlorophene	0.4	(Control)	2900
Hexachlorophene	1.0		2900
Benzethonium chloride	0		2900
Benzethonium chloride	0.5		10,000
Perfume	0		500
Perfume	3.5	(Control)	2900
Perfume	5.0		3700

poses, the viscosity of the concentrate suspension will determine whether conventional liquid filling equipment can be used or if a more costly and possibly less accurate cream filling system must be employed.

Lot-to-lot variations in fumed silica may produce suspensions of different viscosity (Table II). These differences may be caused by variations in the surface area of the fumed silica from lot to lot which could produce different thickening efficiencies. It might also be caused by different amounts of adsorbed moisture in the fumed silica. This would affect the degree of dispersion, under the same conditions of shear.

Table II
Effect of Lot Variations on Viscosity

Ingredient	Concentration (%)	Lot No.		Viscosity (cps)
Isopropyl ester	60.0	A	(Control)	2900
Isopropyl ester	60.0	B		3450
Isopropyl ester	60.0	C		5500
Fumed silica	4.0	A	(Control)	2900
Fumed silica	4.0	B		3800

The viscosity of the concentrate system is also considerably affected by the final concentration of water. Water can be contributed to the system from the aluminum chlorhydroxide, the fumed silica (to a lesser extent), and under humid conditions from the atmosphere. Because of the hygroscopic nature of the concentrate suspension and some of its components, moisture control is very difficult in manufacturing. An example in Table I illustrates how the viscosity of a suspension increases as water is added in 0.5% increments. The initial concentration of water was determined by a modified Karl Fischer technique.

Lot-to-lot variations in isopropyl ester frequently produce large variations in viscosity (Table II). Attempts to determine analytically the differences between the three lots presented were not successful. No contamination could be detected through gas chromatography.

The concentration of aluminum chlorhydroxide in suspension will influence the viscosity of the concentrate system as shown in Table I. Viscosity increases with increasing concentrations of aluminum chlorhydroxide.

In addition, the particle size distribution of the aluminum chlorhydroxide will also influence viscosity. As the particle size distribution includes smaller particles, the viscosity increases. In Table III, 70% of

Table III

Effect of Particle Size Distribution on Viscosity

Grade of Aluminum Chlorhydroxide	Concentration (%)	Particle Size Distn. (%)			Viscosity (cps)
		0–5μ	5–10μ	>10μ	
Impalpable	33	6.4	25.3	68.3(control)	2900
Ultrafine	33	8.8	66.2	25.0	6700

the particles contained in the impalpable aluminum chlorhydroxide suspension are above 10 μ. Seventy-five per cent of the particles contained in the ultrafine aluminum chlorhydroxide suspension are below 10 μ.

Additives to the suspension will influence the viscosity in different degrees. Phenolic antibacterials, for instance, do not seem to have any effect on viscosity, as illustrated in Table I. Quaternary antibacterials, on the other hand, have a marked effect. In Table I, a comparison of suspensions with and without benzethonium chloride at 0.5% by weight is presented.

Perfume as an additive will significantly influence viscosity. An example is given in Table I of the effect of a custom perfume at different levels in the concentrate suspension.

SUMMARY

As illustrated, the concentrate suspension system is very sensitive to water content. Water is an additive to the suspension and acts as a bridging compound between the fumed silica particles that will increase the cell-like structure. Perfumes contain many polar ingredients that may also act as bridging compounds, thus increasing viscosity. In general, additives to the suspension should be screened carefully in order to avoid excessive viscosity. This will provide a broader base for the tolerance of water.

The effect on viscosity of all the variables is cumulative. The viscosity threshold level can easily be exceeded when two or more variables contribute their viscosity increasing influence.

In screening possible suspending media for suspensions containing fumed silica, polarity is the most important factor. If the medium is completely nonpolar, the viscosity will increase at a given concentration of fumed silica. This is due to the fact that the influence of additives becomes greater. Mineral oil, for example, produces concentrate suspensions which have a thick paste-like consistency. More polar suspending media produce lower viscosity. They tend to hydrogen bond with the fumed silica, depressing the formation of the cell-like structure. Ethyl alcohol is an example of a polar suspending medium which produces a very low viscosity. Considerations other than viscosity must be taken into account, however, in choosing a concentrate suspending medium. Mineral oil, for instance, is unacceptable at this concentration in an aerosol form for aesthetic properties and potential inhalation hazard. Ethyl alcohol may cause agglomeration in the finished aerosol product. Isopropyl esters are medium polar to nonpolar in character, provide acceptable finished product characteristics, and usually produce low viscosity concentrate suspensions, but should be expected to vary from lot to lot.

Particular attention should be paid to the concentration of aluminum chlorhydroxide used and the particle size distribution of the sample. The product should contain enough aluminum chlorhydroxide to be efficacious and have a small enough average particle size to provide aesthetic value and to insure proper operation of the aerosol container. However, the viscosity of the concentrate system should be maintained below the threshold level to prevent manufacturing problems.

These discussions have centered around the problems which exist in the formulation of suspension concentrates related to viscosity control. In the finished aerosol form there is no problem with viscosity. This is mainly due to the dilution of all ingredients approximately by a factor of 10.

ACKNOWLEDGMENT

The authors gratefully acknowledge the services provided by the Analytical Chemistry Department of the Gillette Toiletries Company.

(Received June 18, 1970)

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