

Studies of New Aluminum Compounds for Antiperspirant Use. I

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Synopsis—The synthesis of two new groups of alcohol-soluble aluminum compounds is described. They are (a) iron-free hydroxy aluminum alkoxy chlorides, and (b) new ring compounds called chlordioxalumulanes and chlordioxaluminanes. Three species were studied for use in aerosol antiperspirants. All three are mildly acid and appear to be completely safe. Quantitative measurements of antiperspirant effectiveness of aerosols show effectiveness on a par with the best nonaerosol products in the case of two of the three compounds. Fabric destruction data are presented, as are stability and preliminary formulation studies. Aerosols prepared from all three form stable systems free from gelation and precipitation at 7°C or 43°C.

INTRODUCTION

The wide consumer acceptance of a well formulated aerosol-dispensed product has been aptly demonstrated by the dramatic rise of the leading aerosol deodorant to dominate the market for all types of personal antiperspirant deodorants. Aerosol antiperspirants, too, will find a receptive public if effective, properly formulated, and well packaged. In 1965 a program was initiated to evaluate new aluminum compounds which could make possible the formulation of effective aerosol antiperspirants with a high degree of consumer acceptance. This is a progress report on a continuing project.

Prussin (1) stated, "The problem of achieving an effective aerosol antiperspirant spray is considerably more complex. When aluminum

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salts were considered as perspiration inhibitors, it was found that problems of solubility, as one approached effective salt concentration, were encountered."

Thus, the new chemicals to be described were specifically created for aerosol antiperspirant use, although some will find usefulness in more traditional formulations, such as creams, plastic spray bottles, roll-ons, pads, powders, gels, and possibly new forms not presently in vogue.

Since the aerosol technique was perfected in the 1940's there have been many attempts to develop effective antiperspirant systems based on aluminum salts. Aluminum phenolsulfonate, because of its solubility in ethanol, was perhaps the first to be used commercially. Several recently introduced aerosol products contain it as the active ingredient. Kennon (2), in a scholarly review of antiperspirant deodorants, suggested that this salt is ineffective. In 1958, Brown and Govett (3) proposed aluminum chlorhydroxy ethylate, $\text{Al}_2(\text{OH})(\text{OC}_2\text{H}_5)_4\text{Cl}$, which has not been successfully commercialized. Neuman and Koettler (4) advocated aluminum alkoxy chlorides such as $\text{Al}_2(\text{OR})_5\text{Cl}$ or $\text{Al}(\text{OR})_2\text{Cl}$. These compounds, however, are quite insoluble in anhydrous ethanol. Icken and Jahren (5) suggested a mixture of aluminum bisethoxy ethoxide and aluminum nitrilotriethoxide. Both compounds are insoluble in water but hydrolyze to yield alkaline reaction products. Their antiperspirant effectiveness is not known.

Slater, Jass, and Ugelow (6) advocated heating aluminum chloride or basic aluminum chloride, such as $[\text{Al}_2(\text{OH})_5\text{Cl}]_n$, with glycols and subsequent drying to render the compositions soluble in ethanol. Infrared studies made on samples of an aluminum chlorhydroxide complex-propylene glycol product (7) showed new hydrogen bonds involving both primary and secondary groupings of the glycol and the hydroxyls of the aluminum salt. These were not present in the spectra of either component. This suggests a new compound, although one perhaps of some inherent instability.

The Ideal Antiperspirant Compounds

At the outset, it might be useful to try to state the attributes of the so-called ideal antiperspirant compound for aerosol use.

- (a) It should be safe and should not cause dermal irritation from daily use nor be toxic if accidentally swallowed or sprayed in the eyes.

- (b) It must effectively reduce perspiration flow in the axillae.
- (c) It should be cosmetically acceptable with no objectionable odor or color of its own.
- (d) It should not cause corrosion of cans or stress cracking of plastic containers such as polyacetal copolymers.
- (e) It should not cause severe damage to clothing even when the latter is ironed without washing.
- (f) It should be soluble in anhydrous ethanol and form homogeneous systems with fluorocarbon propellents.
- (g) The aerosols made from it must be stable as a function of time and should not gel or precipitate under the wide conditions of storage normally encountered.
- (h) Aerosol valves and actuators should not clog during normal use.
- (i) Perfume materials used should not degrade in odor properties nor give rise to objectionable color.
- (j) The film or residue remaining on the skin must not be too "oily," or too dry, or too tacky.
- (k) The cost of the product must be reasonable.

HYDROXY ALUMINUM ALKOXY CHLORIDE

Most of this experimental work has centered around two new and different systems of aluminum compounds. The first, which is illustrated in Fig. 1, are new iron-free hydroxy aluminum alkoxy chlorides (HAAC) made principally by reacting iron-free distilled liquid aluminum isopropoxide (AIP) with high-purity dry aluminum chloride hexahydrate crystals in anhydrous ethanol. Additional reactant water may be added as a solution in ethanol. The reactions which are carried

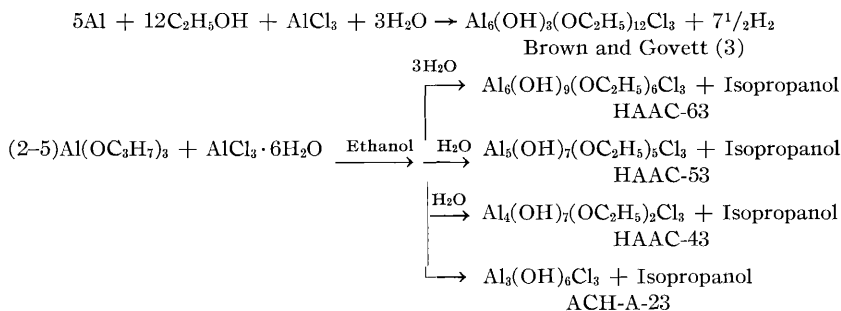


Figure 1. Formation of iron free hydroxy aluminum alkoxy chlorides

Table I
 Typical Analyses of Hydroxy Aluminum Alkoxy Chlorides

Entity	Designation			
	ACH-A-23 25% w/w Soln.	HAAC-43 Gran. Solid	HAAC-53 Gran. Solid	HAAC-63 Gran. Solid
Al ₂ O ₃ , %	13.3	48.3	44.0	42.8
Cl, %	9.3	25.0	17.4	14.9
Ethoxyl, %	...	23.2	34.0	40.7
Iron (Fe), %	0.0004	0.0014	0.0015	0.0015
Heavy metals (Pb), %	<0.0005	<0.0020	<0.0020	<0.0020
Sulfates, % (SO ₄)	0.0002	0.0007	0.0008	0.0007
pH	3.8	4.0	4.1	4.2
Al:Cl atomic ratio	3:3	4:3	5:3	6:3

out at reflux temperatures are highly exothermic and proceed until equilibration takes place. Filtration is carried out to remove trace insolubles. All have a higher hydroxyl and lower alkoxy content than that described by Brown and Govett (3). Moreover, the compounds are of a high order of purity and exhibit excellent stability both in alcoholic solution and combined with propellents in aerosol systems.

When two moles of AIP are reacted with one of aluminum chloride hexahydrate, the composition is essentially a solution of an aluminum chlorhydroxide complex (two-thirds basic) $[Al_3(OH)_6Cl_3]_n$ (ACH-A-23) in anhydrous ethanol and isopropanol. When ACH-A-23 solution is vacuum dried, the resulting solids are water soluble but not completely soluble in anhydrous ethanol. The original solution is a highly effective antiperspirant.

When the other members of the series of HAAC compounds having an aluminum to chloride atomic ratio of 6:3, 5:3, or 4:3 are vacuum dried, the resulting granular solids are completely soluble in anhydrous ethanol and form stable systems with aerosol propellents. Analyses of typical samples are shown in Table I.

The two compounds which have received the most study are ACH-A-23 and HAAC-53. Drying removes the bulk of the isopropanol; however, small amounts remain either as part of the alkoxy groups or as alcohol of crystallization. Gas chromatographic studies of dried HAAC-53 indicate an ethoxyl to isopropoxyl weight ratio of about 14 to 1. The pH of a 5% solution of granular HAAC in water ranges from about 3.9 for ACH-A-23 to about 4.2 to 4.3 for HAAC-63.

CHLORDIOXALUMOLANES AND DIOXALUMINANES

A second group of new chemical entities not heretofore described in the literature has been synthesized. Primarily, the compounds are derivatives of: (a) 2-chloro-1,3,2-dioxalumolane and (b) 2-chloro-1,3,2-dioxaluminanes. They are five- and six-member ring compounds respectively. Three species are shown in Fig. 2 together with the preferred method of preparation. They are reaction products of the

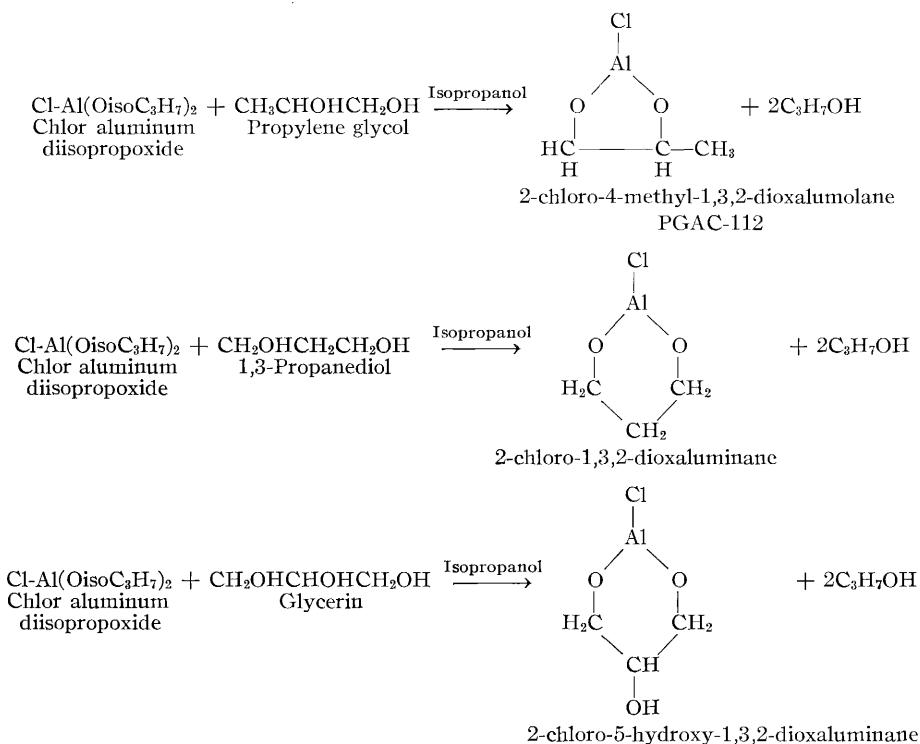


Figure 2. Chlordioxalumolanes and dioxaluminanes

liquid form of chloraluminum diisopropoxide with glycols, substituted glycols, glycerols, and polyhydric alcohol. The potential number of such compounds is almost limitless. That prepared from propylene glycol is perhaps the most economical and most efficacious for aerosol use. It has been called PGAC-112. The third compound shown, 2-chloro-5-hydroxy-1,3,2-dioxaluminane, is derived from glycerin and may be dried and pulverized to a soft relatively nonhygroscopic astringent powder which appears to be useful in dry mildly acid astringent

preparations for the feet or comfort powders for body use. In this respect it is an improvement over pulverized aluminum chlorhydroxide complex, which is literally a pulverized soluble glass.

PGAC-112(2-Chloro-4-Methyl-1,3,2-Dioxalumolane)

The properties and typical analysis of PGAC-112 granular solid are shown in Table II. In practice, the actual purity of the compound may be reduced to about 90%. The balance is principally isopropoxyl groups which are present to the extent of $\frac{1}{4}$ mole per mole of compound. Because of the high purity of the reactants (gaseous HCl gas, distilled aluminum isopropoxide, isopropanol, and propylene glycol) the resulting compound which precipitates in crystalline form is extremely pure. Iron, copper, lead, and other metals are present in trace amounts only. The crystalline precipitate is dried from the bulk of solvent isopropanol to a dry, free-flowing granular powder in a rotary vacuum dryer. It is odorless and dissolves readily in cold or warm anhydrous ethanol to form clear solutions. For aerosol use, filtration is indicated to remove trace insolubles.

The assigned structure is based in part on infrared studies, carefully carried out chemical preparative techniques, and chemical analytical methods. PGAC-112 has been prepared by a method not starting with a glycol as a reactant. Studies of the fundamental structure of PGAC-

Table II
Typical Analysis of 2-Chloro-4-Methyl-1,3,2-Dioxalumolane (PGAC-112)

Aluminum oxide (Al ₂ O ₃)	33.6%
Chlorides (Cl)	23.4%
Al:Cl atomic ratio	1:1
Iron as Fe	0.0012%
Heavy metals as Pb	<0.0010%
pH (1 pt + 20 pts H ₂ O)	3.8

Table III
Oral Toxicity in Mice

Antiperspirant Compound	LD ₅₀
PGAC-112	Male mice, 7.5 g/kg Female mice, 6.7 g/kg
HAAC-53	Male mice, more than 8.0 g/kg Female mice, more than 8.0 g/kg
ACH-A-23	Male mice, more than 10.0 g/kg Female mice, 9.7 g/kg

112 and other members of the series are continuing in several laboratories and will be reported when sufficiently complete.

When PGAC-112 is reacted with water at room temperature, hydrolysis takes place with formation of an aluminum chlorhydroxide and propylene glycol. This apparently occurs on the skin before the component functions as an antiperspirant. In finely divided powder form PGAC-112 has been observed to deliquesce rapidly in air of average humidity. This may help to alleviate actuator clogging.

Compounds Selected for Detailed Study

Of the various compounds shown in Figs. 1 and 2, three were selected for more detailed study. These include: (a) ACH-A-23, a 25% w/w solution of $[Al_3(OH)_6Cl_3]_n$ containing 13.3% Al_2O_3 in a mixture of 43.5% ethanol and 31.5% isopropanol; (b) HAAC-53A, a granular solid containing 44% Al_2O_3 having the formula $Al_5(OH)_9(OC_2H_5)_6Cl_3$; and (c) PGAC-112, a granular solid containing 33.6% Al_2O_3 .

The studies include: (a) pharmacological tests; (b) quantitative assessment of antiperspirant effectiveness; (c) fabric destruction; (d) stability of compounds; (e) stability of aerosols; (f) effect of addition of water on aerosol stability and its effect on the stability of perfumes; (g) formulation studies to determine best propellant system, necessity for additives, valve type, and orifice size, character of spray residues, character of spray, valve and actuator clogging potential; and (h) buffering effect of aluminum nitrilotriethoxide (ANE) on aerosols prepared with PGAC-112. A discussion of corrosion problems related to container selection will also be included.

PHARMACOLOGICAL TESTS

Oral toxicity data are summarized in Table III. On this basis, it is concluded the three compounds would be rated nontoxic. The oral toxicity tests were carried out on vacuum dried samples which were dissolved in water. Since HAAC-53 has a limited solubility in water, it was not possible to introduce more than 8.0 g/kg into the stomachs of the mice.

Skin irritation tests were conducted on abraded and intact rabbit skin. At the 24 and 72 hr readings, no evidence of irritation was observed for any of the three compounds. (Solutions were applied as a 25% w/w solution in anhydrous ethanol, or in the case of ACH-A-23, as an anhydrous mixture of 43.5% ethanol and 31.5% isopropanol.)

Table IV
Eye Irritation^a from Aerosol Sprays

Compound	Condition of Test		
	No Wash	Wash after 2 sec	Wash after 4 sec
PGAC-112	Slight redness in 3/3 rabbits; complete recovery 7 days	Slight redness in 1/3 rabbits; recovery 4 days	Slight redness in 2/2 rabbits; recovery 2 days
HAAC-53	Slight redness in 3/3 rabbits; recovery 3 days	Slight redness in 1/3 rabbits; recovery 2nd day	Much redness in 1/2 rabbits; slight redness in 1/2 rabbits; recovery 4 days
ACH-A-23	Irritation in 0/3 rabbits	Irritation in 0/3 rabbits	Slight redness in 2/2 rabbits; recovery 4 days

^a Irritation concerns only conjunctiva and nictitating membrane; no damage to cornea or iris was observed.

Eye irritation tests were carried out on albino rabbits on aerosols prepared from the three active ingredients containing about 3% w/w Al_2O_3 . While the eye was held open, an actively spraying aerosol was passed slowly twice across the eye of eight rabbits for each sample at about a 15 cm distance. The spray rate was about 0.5 g/sec. The rabbits showed mild displeasure. Following exposure, three rabbits received no further treatment, three were washed after 2 sec with 20 ml lukewarm tap water, and two were washed with the same amount of water after 4 sec. Eye irritation was graded at 1, 2, 3, 4, and 7 days according to Draize. The results are shown in Table IV. Irritation was limited to the conjunctiva and nictitating membrane. The least irritating was ACH-A-23. The slight redness that developed disappeared in about 4 days. Washing after 4 sec was not better than no washing.

ANTIPERSPIRANT EFFECTIVENESS

Because of the wide variation in the sweat output of individuals and in the response to locally applied aluminum salts as inhibitory agents, the pad method is generally considered as quite reliable, especially when carried out by experienced people with careful attention to details. On reviewing the various methods (8-16) and much of the literature on sweating, one soon realizes that it is a very complex phenomenon. For example, Randall *et al.* (17) concluded that "the onset of sweating during progressive elevation of ambient temperatures is influenced by both surface and internal temperatures but is not

controlled exclusively by either." Dobson (18) found that sodium reabsorption takes place in the eccrine ducts while sweat rates remain unaffected.

The antiperspirant effectiveness studies of ACH-A-23, HAAC-53, and PGAC-112 were carried out by Hill Top Research, Inc.,* on aerosols containing about 3% w/w Al_2O_3 of each aluminum compound on the basis of total aerosol weight. Each aerosol contained 45% w/w propellant 12/114 (40/60 blend), the balance being ethanol SDA 40 anhydrous. The formulations were packed in 4-oz plastic-coated glass bottles equipped with Precision† 025/013/0.18 vapor tap valves (YL57255) and mechanical breakup, reverse taper actuators(0.16).

Procedure

A panel of eight women was enrolled as subjects for each test. They were required to abstain from the use of antiperspirants for one week prior to the test. Control sweat collections were made on Friday and the following Monday and Tuesday. The first application was made after the collection on Tuesday. Additional applications were made prior to sweat collections on Wednesday, Thursday, and Friday. All treatments were made by the technician conducting the test. Applications were made by spraying the axillary area for 2 sec from a distance of 15 cm. Of the eight subjects treated with each sample, four were treated on the left axillae and four on the right.

Sweating was induced by seating the subjects in a room maintained at $37.5 \pm 1^\circ\text{C}$ at a relative humidity of 35%. During the first 40 min of the sweat stimulation period, the subjects held unweighed pads of "Webril"‡ (nonwoven cotton padding fabric) in their axillae. This preliminary warm-up period was followed by two successive 20-minute collection periods, during which the subjects held weighed pads of Webril in the axillae. These pads were weighed in tightly capped polystyrene vials before and after use. Tests subjects were allowed to drink ice water as desired throughout the collection procedure.

Results

The mean reductions in sweating resulting from applications of each test material are shown in Table V.

* Miamiville, Ohio.

† Precision Valve Corp., Yonkers, N. Y.

‡ Kendall Mills, Durham, N. C.

No evidence of irritation was observed at any time after application of the test materials. For comparison, commercial nonaerosol antiperspirants yield about 35% reduction when tested as described above. It is possible that the plateau of effectiveness was not reached in four applications, especially in the case of PGAC-112. It would also appear that the lag in response to aerosol-applied anhydrous aluminum compounds is greater than for rubbed-in aqueous based products.

Table V
Antiperspirant Effectiveness

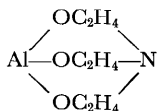
Aerosol Ingredient	Mean Reductions in Sweating Standard Errors of Means at 95% Confidence Levels			
	Second	Third	Fourth	All Values
ACH-A-23	34.0 ± 13.2	29.6 ± 12.9	32.6 ± 12.7	32.8 ± 7.0
PGAC-112	26.0 ± 10.0	30.6 ± 9.9	34.5 ± 7.2	30.6 ± 4.4
HAAC-53	12.9 ± 11.8	19.0 ± 10.8	20.8 ± 10.0	17.6 ± 6.9

FABRIC DESTRUCTION

To find the extent of possible damage to cotton fabric when clothing contaminated with the new aluminum antiperspirant compounds is ironed before washing, the procedure described by Bien (19) of the Good Housekeeping Bureau Laboratory was carried out. Approximately 2.5 g of aerosol substance was sprayed on the 2.54 cm center strip of each 15 × 53 cm pieces of cotton percale. To do this, each aerosol had to be separately calibrated in respect to discharge rate. They averaged about 5 g/10 sec of spray time.

Aerosols were prepared from ACH-A-23, HAAC-53, PGAC-112, and PGAC-112, buffered to pH 4.1 with aluminum nitrilotriethoxide (ANE).^{*} Each contained 5% by weight of active ingredient (AI). Also tested was a new commercial antiperspirant deodorant containing aluminum phenolsulfonate as the active ingredient.

^{*} Aluminum nitrilotriethoxide (ANE) is a white, ethanol-soluble powdered compound having the following structure:



Five pieces of percale were used for each sample. Each was cut into five 10 × 15 cm pieces for breaking. Thus, 25 samples were tested for each antiperspirant. The cotton strips were conditioned and rehydrated in a humid environment for 24 hr before determining the tensile strength, using a Scott tester. The results are shown in Table VI. The alumi-

Table VI
Fabric Destruction Tests
Various Aerosol Antiperspirants

Active Ingredient	Per Cent Loss in Tensile Strength (Percale)
ACH-A-23	12
HAAC-53	None
PGAC-112	7.5
PGAC-112/ANE mol. ratio 1/0.2	None
Aluminum phenolsulfonate	15.5

num phenolsulfonate aerosol is seen to be the most destructive, followed by ACH-A-23 and PGAC-112. HAAC-53 did not decrease the tensile strength under the conditions of the test. Buffering of PGAC-112 with 0.2 M of ANE/M of compound reduced the loss to zero.

STABILITY AND PRELIMINARY FORMULATION STUDIES

Basic Compounds

Solutions (25%) of ACH-A-23, HAAC-43, HAAC-53, HAAC-63, and PGAC-112 in anhydrous alcohol have been stored at 70°C, room temperature, 37.5°C, and 44°C temperatures in 4-oz glass prescription bottles for six months. Observation during this period has revealed the absence of perceptible change—including gelation, precipitation, viscosity characteristics, odor, color, and clarity.

Aerosol Stability

Preliminary stability tests were carried out in 4-oz glass bottles using 50% propellents 11 or 113. The formulas prepared from each active ingredient are shown in Table VII.

Table VII
Composition of Aerosols (Per Cent)

Entity	Sample No.				
	1	2	3	4	5
25% w/w alcoholic solution of Al-salt	20.0	40.0	20.0	20.0	20.0
Ethanol SDA 40	30.0	10.0	23.8	26.8	26.0
Hexachlorophene	0.2	0.2	...
Hexadecyl alcohol	4.0	2.0	4.0
Silicone DC-555 ^a	2.0	1.0	...
Propellent	50.0	50.0	50.0	50.0	50.0

^a Dow Corning Corp., Midland, Mich.

Samples of the above were stored at 7°C room temperature, 37.5°C, and 44°C for more than four months. All samples remained clear. Only ACH-A-23 developed a slight amber color in samples containing hexachlorophene when stored at 44°C.

It was concluded that the new aluminum compounds are stable in respect to gelation, precipitation, color, odor, and viscosity changes when formulated in typical aerosol systems at 5 and 10% active concentration.

The Effect of Water on Stability of Aerosols and on the Stability of Perfumes

It was observed in the early experimental studies that ACH-A-23, HAAC-53, and PGAC-112, in decreasing order, adversely affected the odor of perfume and in many cases caused the formation of intense color or darkness. This was not totally unexpected. It is known that aluminum alkoxides and chlorine derivatives are catalysts for the well-known Meerwein-Ponndorf-Verley reduction of aldehydes and ketones. The compounds are used commercially for this purpose. The problem at hand was to find a suitable inhibitor which is fully compatible with the system. Water was known to be such an inhibitor. The alcoholic solutions of the three chemicals ACH-A-23, HAAC-53, and PGAC-112 are completely anhydrous with only trace amounts of water present. The questions posed were twofold: (a) Would small amounts of water sufficiently inhibit the degradation of odor and the development of color, and (b) how much water can the aerosol systems tolerate without gelling or precipitating?

Experimental

Two sets of aerosols were prepared from each antiperspirant compound with two different and distinct perfume compositions. The general composition was as follows:

Active ingredient (25% w/w solution)	25% w/w
Hexachlorophene	0.25
Perfume	1.0
Myristyl lactate	1.0
Propellant	50.0
Ethanol SDA 40	q.s.
Water	as required

For ACH-A-23 the water content was varied from 0, 2 to 5% by weight; for HAAC-53 the water varied from 0, 1 to 2%. In the PGAC-112 compositions, the water was varied from 0, 2 to 4%. Each variation was made in quadruplicate and individual samples stored at 7°C, room temperature, 37.5°C, and 44°C. Observations were made after one month.

*Results**ACH-A-23*

(a) Remained clear with 0 and 2% water; 5% water caused gelation or precipitation.

(b) With no water there is progressive darkening which is greatest at the higher temperature. The development of color is accompanied by degradation of odor properties.

(c) Two per cent water greatly inhibited color development and odor degradation. Samples stored at 7°C, room temperature, and 37.5°C showed very little change in character.

HAAC-53

(a) Samples containing 2% water gelled; those containing 1% water were unchanged.

(b) In samples containing no water the color intensity was less than in the case of ACH-A-23. Some darkening and odor degradation took place.

(c) In samples with 1% water there was almost no degradation of odor nor development of color.

PGAC-112

(a) Samples containing 4% water either gelled or precipitated.

(b) In samples with no water there was some darkening or slight increase in color intensity; change in odor was minimal.

(c) Samples containing 2% water were unchanged in appearance. Gelation or precipitation did not occur, nor was there a perceptible change in odor or color.

Conclusions

(a) Addition of small amounts of water, *e. g.*, 1% on total weight of aerosol, inhibits the development of color or degradation of odor due to reduction of aldehydes and ketones in perfumes without adversely affecting the physico-chemical properties of the aerosol system.

(b) PGAC-112 and ACH-A-23 aerosol systems (5% active content) can apparently tolerate up to 2% water based on total weight without gelation or precipitation. HAAC-53 systems are apparently more sensitive and cannot tolerate more than 1%.

FORMULATION STUDIES*

Initial compatibility experiments established several facts: (a) Residues remaining on the skin from ACH-A-23 are inherently wetter and "oily," those from HAAC-53 are "dry," and those from PGAC-112 are intermediate. It was considered that ACH-A-23 residues would require little or no additives to improve skin feel and HAAC-53 would require the most. (b) If ACH-A-23 were used, the perfume would have to mask isopropanol which would be present at 6% concentration in the finished aerosol. (c) The concentration of active ingredient solids should be at about the 5% level based on total aerosol weight. (d) Precision 025/013/018 vapor tap valves with mechanical breakup reverse taper actuators (016) were preferable to 018/013/018 size. (e) Propellant 12/114 (25/75) was preferable to 12/11 (50/50).

* Most of this work was carried out in the Freon Products Laboratory of the E. I. du Pont de Nemours Co., Wilmington, Del.

Table VIII
Antiperspirant Formulations Based on HAAC-53 and ACH-A-23

Component	Sample No.							
	7A	1A	2A	3A	11A	12A	13A	14A
HAAC-53 (25% soln.)	20.0	20.0	20.0	20.0
ACH-A-23 (25% alc. soln.)	20.0	20.0	20.0	20.0
Ethanol SDA 40 anhydrous	32.5	32.5	32.5	32.5	34.5	34.5	34.5	34.5
Cetyl alcohol	1.0	1.0	1.0	1.0
Silicone fluid ^a DC-555	0.3	0.3	0.3	0.3
Squalane ^b	0.5	0.5	0.5	0.5
Perfume GD-6763-1 ^c	0.7	0.7	0.7	0.7	0.5	0.5	0.5	0.5
Prop. 12/114 (25/75)	45.0	45.0
Prop. 12/114 (40/60)	...	45.0	45.0
Prop. 12/11 (40/60)	45.0	45.0	...
Prop. 12/11 (50/50)	45.0	45.0

^a Dow Corning Corp., Midland, Mich.

^b Robeco Chemicals, Inc., New York, N. Y.

^c Givaudan-Delawanna, Inc., New York, N. Y.

Table IX
Antiperspirant Formulations Based on PGAC-112

Component	Sample No.					
	1	2	3	4	5	6
PGAC-112 (25% soln. ethanol)	20.0	20.0	20.0	20.0	20.0	20.0
Ethanol	32.8	32.8	32.8	34.6	34.6	34.6
Cetyl alcohol	1.0	1.0	1.0
Silicone fluid DC-555 ^a	0.5	0.5	0.5
Squalane ^b	0.3	0.3	0.3
Perfume GD-6763-1 ^c	0.3	0.3	0.3	0.3	0.3	0.3
Hexachlorophene	0.1	0.1	0.1	0.1	0.1	0.1
Prop. 12/114 (40/60)	45.0	45.0
Prop. 12/114 (25/75)	45.0	45.0
Prop. 12/11 (50/50)	...	45.0	45.0	...

^a Dow Corning Corp., Midland, Mich.

^b Robeco Chemicals, Inc., New York, N. Y.

^c Givaudan-Delawanna, Inc., New York, N. Y.

These initial experiments were followed by studies to determine the best propellant system and effect of some additives on the characteristics of the spray and nature of the residue.

Procedure

Aerosols were prepared in 4-oz plastic coated glass bottles. The formulations are as shown in Table VIII for ACH-A-23 and HAAC-53, and in Table IX for PGAC-112.

Samples were stored for six days at 37.5°C, removed from the oven, and allowed to stand overnight at room temperature. They were tested by spraying on the palm of the hand and evaluating the spray and residue characteristics and returned to the oven. The cycle was repeated four times for ACH-A-23 and HAAC-53. Aerosols with PGAC-112 were cycled five times. The character of the spray and nature of the residue was rated as satisfactory, acceptable, barely acceptable, and unacceptable.

Results

(a) Propellant 12/114 (40/60) was the best choice for all three aluminum compounds.

(b) Color and odor changes from perfume were more noticeable with ACH-A-23, slight with HAAC-53, but absent with PGAC-112.

(c) Propellant 12/11 (50/50) was unsatisfactory for PGAC-112 and ACH-A-23. It can be considered further for HAAC-53 but imparts a greater chilling effect than 12/114 blends.

(d) None of the samples under test gelled or precipitated.

(e) Valves with 0.025 in. orifices are preferable to those with 0.018 in. orifices.

(f) Samples containing propellant 12/114 (40/60 blends) were rated satisfactory throughout the test. Blend 12/114 (25/75) was satisfactory with PGAC-112 containing additives.

(g) HAAC-53 and PGAC-112 require additives to improve skin feel. ACH-A-23 may not require additives for that purpose.

(h) Aerosols prepared with ACH-A-23 and HAAC-53 with propellant 12/11 (40/60 blends) clogged valves and actuators during the first week; the sprays were very wet.

CORROSION PROPERTIES AND CONTAINER SELECTION

Mildly acid halides of all kinds strongly corrode most metals, including iron, aluminum, copper, zinc, and type 304 stainless steel. Pressure and heat increase the rate of such attack. Uncoated steel and aluminum containers are strongly attacked. Studies of aerosols prepared with ACH-A-23, HAAC-53, and PGAC-112 and in epoxy coated aluminum containers show some promise. Studies in double coated steel cans are underway but must be carefully observed. One should expect some attack because coated cans are never totally free of scratches or occasional pin holes.

Based on the data at hand at present the only firm container recommendation is plastic-coated glass with Precision vapor tap valves.

SUMMARY

1. The synthesis and properties of two new groups of alcohol soluble aluminum compounds are described. They are iron-free hydroxy aluminum alkoxy chlorides and novel five- and six-membered ring compounds called chlordioxalumolanes and chlordioxaluminanes.

2. Three species were studied for use as aerosol antiperspirants. They include: ACH-A-23, a two-thirds basic aluminum chloride in anhydrous alcohol; PGAC-112, 2-chloro-4-methyl-1,3,2-dioxalumolane; and HAAC-53— $\text{Al}_5(\text{OH})_7(\text{OC}_2\text{H}_5)_5\text{Cl}_3$. The last two are granular solids.

3. All three form stable, homogeneous, anhydrous systems with alcohol and fluorocarbon propellents.

4. Preliminary pharmacological tests indicate that they are safe.

5. Quantitative determination of antiperspirant effectiveness of aerosols indicates that those prepared with ACH-A-23 and PGAC-112 are on a par with the best commercially available nonaerosol types similarly tested. HAAC-53 effectiveness is positive but about 37% less.

6. Fabric destruction tests indicate that they all show less than 20% loss in tensile strength when tested by the Good Housekeeping Bureau's method and hence pass their test. Actual values were 12%, 7.5%, and no loss for ACH-A-23, PGAC-112, and HAAC-53, respectively.

7. Formulation studies indicate that 5% active ingredient solids is preferable. Also 45% propellent 12/114 (40/60) blend gives the best spray characteristics. Additives are needed to improve skin feel of HAAC-53 and PGAC-112 residues. ACH-A-23 residues are "oilier." Precision vapor tap valves with 025/013/018 mechanical breakup reverse taper actuators (016) have given good performance.

8. Perfume degradation and the development of color have been observed in ACH-A-23, HAAC-53, and PGAC-112, in decreasing order of intensity. Addition of 1% water helps alleviate this without causing gelation or precipitation. Specially designed perfumes that are stable in anhydrous systems have been developed.

9. The pH of anhydrous aerosols prepared with PGAC-112 (pH 3.9) may be increased by the addition of aluminum nitrilotriethoxide (ANE).

10. The use of plastic-coated glass bottles is recommended. Tests with epoxy-lined aluminum containers show promise. The use of

double coated steel cans is considered hazardous on a theoretical basis due to scratches and occasional pin holes which occur in present-day coated steel cans.

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