

KA005301

"FREON" PRODUCTS LABORATORY

E. I. du Pont de Nemours & Company

TECHNICAL REPORT

Report Number: KSS-4966

Subject: Reformulation of "Right Guard" Deodorant

Company: The Gillette Company
Boston, Massachusetts

By: R. P. Ayer

Date: September 10, 1964

Object:

To reformulate "Right Guard" Deodorant with a less expensive propellant than the presently used 45% "Freon-12"/"Freon-114" (57/43) without unfavorably altering the vapor pressure, flammability, spray characteristics and nonchilling (tingling) sensation on the skin according to the following criteria:

Vapor pressure	-	40 psig or less at 70°F
Flammability	-	Flash point over 100°F; flame extension and flashback no longer than "Right Guard" with present valve/actuator combination
Spray characteristics	-	Virtually unchanged
Nonchilling (tingling)- on skin	-	Determined by placing shaving lather formulated with propellant in question on the upper lip and comparing tingling sensation to that of shaving lather formulated with "Freon-12"/"Freon-114" (57/43)

EID10479

KA 005301

- 2 -

Conclusions:

The submitted concentrate can be formulated with either 45% "Freon-12"/"Freon-114"/Vinyl chloride (49/39/12) or 45% "Freon-12"/"Freon-114"/"Freon-11" S/Isobutane (57/27/10/6) and packaged with the presently used valve and actuator at propellant cost savings of approximately 3.5¢/lb and 7.1¢/lb, respectively, compared to "Freon-12"/"Freon-114" (57/43), without unfavorably altering the above mentioned criteria.

Additional propellant cost savings might be achieved by one or more of the following: decrease propellant/concentrate ratio to 40/60, use 5% more "Freon-11" S and 5% less "Freon-114" in the quaternary blend, replace some of the "Freon-114" of the ternary blend with "Freon-11" S. Further cost reduction will mean forfeiting one or more of the desirable characteristics of the present commercial product (at least with the present valve/actuator combination).

Neither the over-all shelf life nor the odor was evaluated for any length of time on these less expensive propellant/present concentrate combinations; however, the odor does not appear objectionable on casual observation and it is known the shelf life is satisfactory with both "Freon-12"/"Freon-11" S and "Freon-12"/"Freon-114". Therefore, any trouble can be pinpointed quickly to vinyl chloride and isobutane, respectively, and an appropriate "Freon-12"/"Freon-114"/"Freon-11" S blend can still effect some cost reduction.

Results:

Experimental work included a quick evaluation of "Freon-12", "Freon-12"/vinyl chloride (85/15) and "Freon-12"/isobutane (95/5) propellents with the submitted concentrate. None are acceptable, because with sufficient propellant to raise the flash point of the aerosol formulation over 100°F, the pressure is higher than 40 psig and the spray characteristics are not desirable.

Considerable evaluation and testing were carried out on "Freon-12"/"Freon-114"/"Freon-11" S/isobutane mixtures in order to have as much "Freon-11" as possible without introducing what, in our opinion, would be an undesirable tingling sensation and to have as much isobutane as possible without adversely affecting the flammability. This was accomplished by choosing the "Freon-12"/"Freon-114"/isobutane (56/34/10) mixture having a vapor pressure of approximately 50 psig at 70°F and introducing

EID10480

Results: (Continued)

"Freon-11" S at 5, 10 and 15% of the total mixture. Every blend was used to prepare aerosol samples for checking the vapor pressure at 70°F, the flammability, spray characteristics, and the tingling sensation. Once the latter reached an upper limit (greater than 10%), in our opinion, for the particular tingling test used, the amount of isobutane was reduced until the flash point, within experimental error, reached 100°F. All the samples contained 45% propellant with the exception of the shaving lather which contained 10%. The tingling sensation and the flash point are the two criteria with most variance among the various blends tested. For extra certainty in keeping the flash point over 100°F, it is recommended the amount of isobutane in the blend be at 6 rather than 7%. It is also recommended "Freon-11" S be used to inhibit the free radical reaction between "Freon-11" and alcohol. The results are summarized in Table I.

Similar experiments, the results of which are summarized in Table II, were carried out with "Freon-12"/"Freon-114"/vinyl chloride mixtures having vapor pressures of approximately 50 psig at 70°F. The amount of vinyl chloride was reduced from 20% of the mixture until the flash point reached 100°F. It is recommended the vinyl chloride be reduced from 13 to 12% of the total to be absolutely certain the flash point is greater than 100°F.

Comments:

Samples for measuring the vapor pressure and determining the flammability were prepared by loading 55.0 g of "Right Guard" concentrate (or anhydrous SDA-40 ethanol) in three-ounce, sideseam (unlined) containers and very carefully purging with "Freon-12" before capping with the submitted vapor tap valves and pressure filling 45.0g of the respective propellents. Vapor pressures were determined on samples thermostatted at 70°F for 30 minutes with a prepressurized gage. Because of the change in composition during spraying with a vapor tap valve, separate samples were used for determining the flash point and flame extension/flashback. Flash point determinations were started when the contents of the aerosols were at -50°F.

The shaving lathers were prepared by loading 90.0g of shaving lather concentrate in four-ounce, plastic-coated glass bottles before purging, capping with a standard Precision valve and pressure filling 10.0g of the respective propellents.

EID10481

Results: (Continued)

The tingling tests were carried out on samples less than one day old by placing foam from a "Freon-12"/"Freon-114" (57/43) sample on one side of the upper lip and foam from the other propellant mixture samples (one at a time) on the other side of the lip and waiting from 2-3 minutes or until some difference or tingling sensation was noticeable. Of the foams tested, only those containing propellant with 15% "Freon-11" were considered unacceptable and those with 10% "Freon-11" were borderline. Assuming this test is extremely sensitive, blends with 15% "Freon-11" S may be satisfactory for the intended end-use.

The propellents used in the preparation of the aerosol samples were first prepared in two-pound cylinders with the exception of "Freon-12"/"Freon-114" (57/43).

In order to conserve concentrate, some of the samples were prepared with anhydrous ethanol. As would be expected, the results of vapor pressure measurements and flammability determinations with either concentrate or alcohol are within experimental error of one another. The vapor pressures were consistently 40 psig or less, and with commercially cold-filled samples, pressures of 1-2 psig less can be expected.

The results of the flammability tests are quite consistent and straightforward. With the exception of flashback in the side position, the propellents suggested for replacement of "Freon-12"/"Freon-114" (57/43) will, when used with a 45/55 propellant to concentrate ratio, give a product which would have a Combustible classification according to the NYCFD flammability regulations for pressurized products just as the present "Right Guard". This is assuming the transitory flashback in the inverted position would be ignored. Unfortunately, the side-position flashback is not short-lived with any of the propellents, including "Freon-12"/"Freon-114" (57/43). Flashback can be eliminated with another vapor tap valve/actuator combination, but it is our experience that those which do this have more powerful, less desirable spray characteristics than does "Right Guard" or the experimental samples with which we were comparing it.

Worthy of future consideration is the fact that the proposed changes to the ICC pressure regulations would allow formulations with pressures up to 160 psig at 130°F to be packaged in sideseam containers. This would include formulations with straight "Freon-12" and with enough of it (40%-50%) to give flash points over 100°F. The spray characteristics would be esthetically less desirable but the flame extension/flashback problem could doubtlessly be balanced to give a Combustible NYCFD classification for the resulting more powerful sprays.

KA005301

Results: (Continued)

Should odor or some other unforeseen problem under either or both isobutane and vinyl chloride unsuitable for use with your present concentrate, further effort can be directed toward a straight "Freon-12" formulation or a "Freon-12"/"Freon-114"/"Freon-11" 3 formulation. The latter blend would be the one having approximately 50 psig vapor pressure at 70°F (so that aerosols could be 40 or under) and the maximum amount of "Freon-11" S which will not give an underarm tingling sensation (probably 10%-15% based on lip test).

Additional effort at reducing the propellant/concentrate ratio to 40/60 would also be worthwhile, regardless of the propellant blend, based on the favorable flash point result (one experiment) with "Freon-12"/"Freon-114" (57/43). The flash point is the limiting factor here and with these nonflammable blends the flash point is essentially a function of the alcohol concentration.

It should be remembered that although the quaternary blend may sound rather ominous, especially to our plant, the "Freon-11" S can be added with the concentrate and the propellant supplied as a ternary mixture of "Freon-12"/"Freon-114" and isobutane.

EID10483

KA005301

Characteristics of Three-Ounce Samples of Freon-12"/
"Freon-114"/"Freon-11" S/Isobutane (1) Propellents and Gillette
"Right Guard" Deodorant Concentrate and Valve/Actuator Combination

Propellant	Tingling (2) Sensation	Vapor Pressure, psig at 70°F	Flash Point, °F	Flame Extension, inches (3)		Flammability	
				Upright Side	Inverted	Upright Side	Inverted
"Freon-12"/"Freon-114" (57/43) Commercial {4-oz} Laboratory {3-oz} Laboratory {4} Laboratory {5}	No	39, 40 40 - -	104, 106 - 102 102	0 0 0 -	9-10 11-12 11-12 10-11	0 0 0 -	4 4 4 4
"Freon-12"/"Freon-114"/ isobutane (56/34/10)	No	40(4)	-	0	12-13	0	4-5
"Freon-12"/"Freon-114"/ "Freon-11"/isobutane (56/29/5/10)	No	40(4)	-	0	12-13	0	5
"Freon-12"/"Freon-114"/ "Freon-11"/isobutane (56/24/10/10)	Perhaps	40(4)	92	0	12-13	0	4-5
"Freon-12"/"Freon-114"/ "Freon-11"/isobutane (56/19/15/10)	Yes	40(4)	-	0	11-12	0	4-5
"Freon-12"/"Freon-114"/ "Freon-11"/isobutane (56/26/10/3)	-	-	95	-	-	-	-
"Freon-12"/"Freon-114"/ "Freon-11"/isobutane (56/27/10/7)	-	37	102	0	10-11	0	4
"Freon-12"/"Freon-114"/ "Freon-11"/isobutane (56/24/10/7)	No	39, 39	98, 100	0	12-13	0	4-5

EID10484

KA 005301

- 7 -

Notes for Table I:

- (1) Phillips Petroleum Company (A-31)
- (2) Lip test with 10% propellant in shaving lather* Compared to "Freon-12"/"Freon-114" (57/43)
- (3) Fall to zero as soon as standpipe liquid exhausted
- (4) SDA-40 anhydrous alcohol substituted for "Right Guard" concentrate
- ((5) Sample consisted of 60% concentrate, 40% propellant

* Stearic acid	7.06 Wt %
Coconut fatty acid	1.72
Triethanolamine	4.40
Glycerine	2.00
Water	84.82

EID10485

TABLE I KA 005301
 Characteristics of Three-Ounce Samples Prepared with 4% Freon-12/
 "Freon-114"/Vinyl Chloride (1) Propellents and Gillette "Right
 Guard" Deodorant Concentrate and Valve/Actuator Combination

Propellant	Tingling Sensation (2)	Vapor Pressure, psig at 70°F	Flash Point, °F	Flame Extension, inches		Flammability	
				Upright	Inverted	Upright	Inverted (3)
"Freon-12"/"Freon-114"/ Vinyl chloride (45/35/20)	Perhaps	37	84	-	-	-	-
"Freon-12"/"Freon-114"/ Vinyl chloride (48/37/15)	Perhaps	38	94	-	-	-	-
"Freon-12"/"Freon-114"/ Vinyl chloride (49/38/13)	No	40	102	0	14-15	0	5

Notes: (1) Matheson Company, Inc. (inhibited vinyl chloride)

(2) Lip test with 10% propellant in shaving lather* compared to "Freon-12"/"Freon-114" (57/43)

(3) Falls to zero as soon as standpipe liquid exhausted

* See Table I

KA 005301