

"FREON" PRODUCTS LABORATORY

E. I. du Pont de Nemours & Company

100-05051

TECHNICAL REPORT

Report Number: KSS-4736

Subject: Reduced Cost Hair Spray Formulations

Company: Zenith Chemical Company
Newark, New Jersey

By: R. P. Ayer Date: April 7, 1964

Object: To evaluate, run flammability tests and compare prices of hair sprays formulated with "Freon-12"/"Freon-11" (40/60), vinyl chloride/isobutane and isobutane/fluorocarbon propellant blends having the same vapor pressure. Basis for comparison is 65% "Freon-12"/"Freon-11" (40/60) formulation packaged with submitted concentrates (one cent per ounce) in sixteen-ounce container equipped with submitted valves and actuators.

Conclusions:

The 55% and 65% propellant formulations have better spray quality than 45% ones with all three valves and actuators. Final selection is a matter of personal choice. For any given propellant concentration, the cost per unit decreases in the order: "Freon-12"/"Freon-11" (40/60), "Freon-12"/"Freon-11"/Isobutane (35/56/9), "Freon-12"/"Freon-11"/Vinyl Chloride (25/57/20). The valve/actuator combinations, presumably selected for their ability to give an "acceptable" spray with less than 65% propellant, give gentle sprays having short flame extensions but measurable flashback (in virtually every case). This net result is, according to our interpretation of the NFPA regulations pertaining to aerosols, that most of them will be classified as Extremely Flammable, whereas without the flashback, they would be classified Combustible. All flash points are above 100°F. Vinyl chloride is not recommended for use in hair sprays because of questionable toxicity and shelf life considerations.

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results:

The three blends of fluorocarbon and isobutane/fluorocarbon were evaluated for their ability according to two criteria: vapor pressure at 70°F. as compared to "Freon-12"/"Freon-11" (40/60), i.e., 30.5 psig, and combustibility. All three blends just below the "lower flammability limit" (and well below their compositions which do not form explosive mixtures in the air completely vaporized). The two of interest meeting these criteria were: "Freon-12"/"Freon-11"/Vinyl Chloride (25/57/18); and "Freon-12"/"Freon-11"/Isobutane (35/56/9).

The relative savings, cents per sixteen-ounce canister (8.33 gals. 100% pure) with our "approximate" bulk prices for the propellant and our suggested approximate prices of one cent per ounce, compared to the "Freon-12"/"Freon-11" (40/60) formulation are presented in Table X.

The actual formulations evaluated and the corresponding vapor pressure and flammability data are summarized in Table XI.

APPENDIX

Analysis of three propellant/concentrate combinations was attempted with the three propellants in order to have a sample of "low propellant" and three of three concentrate/propellant ratios. Formulations lower than 1/1 propellant were judged unlikely to produce a spray with spray characteristics of the 1/1 samples.

Vapor pressure was measured, and the flammability tests were carried out according to the NFPA regulations with the exception that one of the samples was sprayed in the side position and not down. In addition, vinyl chloride or isobutane were sprayed in the front position. The flash point of hair spray formulations is of little concern if the blend is nonflammable. The flash point of the "Freon-12"/"Freon-11" (40/60) blend is "below limit" because the flash point of the blend is below the flash point of alcohol. Concentration of alcohol in the blend is 60%-65%, the total flash point of the blend is below 100°F.

As far as valves go, your three valves are correct. The valves will be below 1/2 inch in size so this is of little concern.

When it comes to the valve is another matter. The handle was a matter of varying degrees. After determining the valve will suit the "basic" valve/actuator combination, other combinations were tried for the following reasons.

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The "Freon-12"/"Freon-11" and "Freon-12"/"Freon-11"/Vinyl Chloride samples showed minimum flashback with the 016/0135 valve and 015 (RKN-63) actuator, regardless of the formulation. Therefore the RKN-63 actuator was arbitrarily tried on the 65% formulation having the 016/018 valve and on the 45% formulation having the 016/025 valve in order to see if flashback was likely to be reduced by other combinations. In no case was the flashback changed by switching actuators. The trend was similar but not so pronounced with the isobutane samples. Here, we arbitrarily tested those formulations (and valves) giving one inch (the minimum observed) flashback with the other two actuators. In no case was the flashback changed.

The relative savings in material costs per unit are obvious from Table II. Your judgment of how flammability classification, performance, and expected shelf life and toxicity will influence acceptance of your product may, and probably should be, however, the deciding factor for which formulation or formulation are chosen. For this reason, we would like to point out several facts. High quality bias tape is available formulated with "Froon-12"/"Froon-11" and especially with "Froon-12"/"Froon-11" & propellant have excellent shelf life. Nevertheless, for some types of loading and excellent performance, the latter is usually depending on very fastness. Admittedly, and unfortunately, the above classification is not generally acceptable, with or without reference to propellant, and flashback of varying degree and one must experiment with many valves and actuators before finding a "suitable" one. Ignoring flashback and its influence on NICEO flammability classification, very serious consideration must be given to changing the ability of your product either by using liver propellant (with low and good one), or introducing more flameless and less tested compounds like "Froon-12"/"Froon-11". As you may or may not be aware, the effect of these low vapor pressures normally used in this case is that only a 10% amount tolerate more than 50% reduction of the flame. This is a very "complete" non-flammable; therefore, all the "Froon-12"/"Froon-11" compounds will be allowed to transport and store with no real safety against flash chamber or flash-back during use. These are not now currently shipping vinyl chloride, and it is a very serious problem. In addition, the use of these compounds in the field is hazardous and storage is also a very serious problem.

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Comments: (continued)

The toxicity situation of vinyl chloride still is sufficiently unclear that we do not recommend it for products which are normally used around the face because inhalation will occur to some extent. We are certain that it is at least 100% more toxic than either "Freon-12" or "Freon-11".

The shelf life of hair sprays packaged with "Freon-12"/"Freon-11" (or "Freon-11" S) is excellent and has been extensively studied. The primary reaction occurring is a free radical reaction between "Freon-11" and alcohol, which can be nearly eliminated or controlled with inhibited "Freon-11". Nevertheless, the possibilities for polymerizing or copolymerizing vinyl chloride under these conditions, or others for that matter, are real. Until such time that extensive storage stability data indicate a highly satisfactory shelf life for vinyl chloride-containing hair sprays, it seems unwise to experiment with the most successful of all aerosol products.

TABLE I

Relative Savings in Cents per 430 Gram Fill of Formulations Compared to 35% Concentrate-65% "Freon-12"/"Freon-11" (40/60) Propellant

<u>"Freon-12"/"Freon-11" (40/60)</u>	
0.5%	55%
0.00	0.64
	1.27
<u>"Freon-12"/"Freon-11"/Isobutane (35/55/9)</u>	
0.5%	55%
1.05	1.53
	2.02
<u>"Freon-12"/"Freon-11"/Inhibited Vapors (23/57/20)</u>	
0.5%	55%
2.13	2.44
	2.73

Valves and Actuators (1) Vapor Pressures
and Flammability Data of Hal. Spray Formulations

"Freon-12"/"Freon-11" (40/60)

Formulation	Valve	Actuator	Vapor Pressure, psig at 70°F	Flame Extension, inches	Flashback, inches	Flash Point, °F
5% Propellant	016/018	020	30	9	3	131, 134
"	"	015 NP	"	"	3	"
"	016/0135	015 NP	30	9	3	"
"	016/025	015	30	7	3	"
5% Propellant	016/018	020	26	9	2	129, 127
"	016/0135	015 NP	26	10	0	"
"	016/025	015	26	11	1	"
5% Propellant	016/018	020	22	9	3	115, 118
"	016/0135	015 NP	23	12	1	"
"	016/025	015	23	10	2	"
"	"	015 NP	"	"	2	"

"Freon-12"/"Freon-11"/Isobutane (35/55/10)

5% Propellant	016/018	020	30	9	(2)	129, 131
"	016/0135	015 NP	30	7	3	"
"	016/025	015	30	0	4	"
5% Propellant	016/018	020	28	7	4	110, 113
"	016/0135	015 NP	28	8	1	"
"	"	015	"	"	1	"
"	"	020	"	"	1	"
"	016/025	015	28	8	3	"

