FREON PRODUCT INFORMATION

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AN EMPIRICAL METHOD FOR EVALUATING THE SPRAY CHARACTERISTICS OF AEROSOL PRODUCTS

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EVALUATING THE SPRAY PROPERTIES OF AEROSOL PRODUCTS

AN EMPIRICAL METHOD FOR

by Dr. Paul A. Sanders, "Freon" Products Division, E. I. du Pont de Nemours & Company

The spray characteristics of aerosol products vary from wet, streamy sprays to very fine sprays, depending upon the application for which the aerosol was designed. Wet or coarse sprays are desirable for residual products such as residual insecticides, while sprays with a fine particle size are necessary for space aerosols, such as room deodorants. The type of spray produced by an aerosol product is one of its most important properties.

The aerosol chemist has a wide variety of propellants, propellant blends, and solvents available for the formulation of aerosol products. Sometimes this profusion of propellants and solvents presents a problem to the formulator who must attempt to achieve the desired spray characteristics while keeping in mind such factors as pressure, compatibility, flammability, and cost. Quite often, for various reasons, it is desirable to replace the original propellant that was used in an aerosol product with a different propellant, while maintaining the original spray properties of the aerosol.

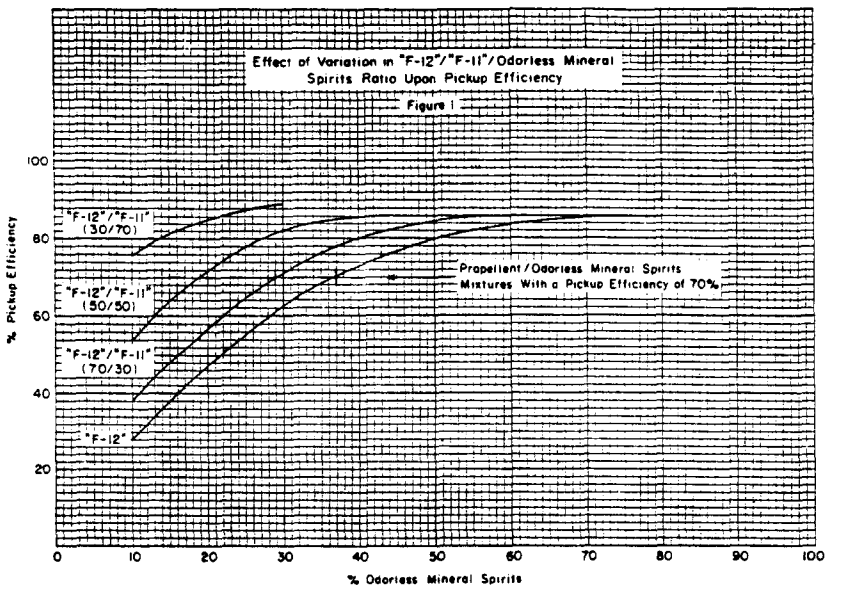
Up to the present time there has been no simple method for comparing the spray properties of an aerosol product that has been formulated with different propellants. A method for determining the particle size distribution of space insecticides has been published (Reference 1), but this procedure is applicable only for products formulated with high-boiling solvents, such as deodorized kerosene. In addition, the method is time consuming and requires expensive equipment.

A comparatively simple method has been developed for comparing the spray characteristics of an aerosol product when the concentrate has been formulated either with different propellants or with different concentrations of the same propellant. One of the most practical applications of the method is that it may be used to determine what concentrations of different propellants will produce about the same spray properties. The method is useful for products formulated either with high-boiling solvents such as kerosene or odorless mineral spirits, or lower boiling solvents, such as ethyl alcohol. Data which illustrate this method for evaluating the spray characteristics of aerosol products are given in the present paper and the potential applications and limitations of the method are discussed.

General Discussion

The method presented in this paper for comparing the spray characteristics of aerosol products is based upon a modification and extension of the "Tentative Method for Determining Pickup Efficiency of Residual Aerosol Insecticides", which was adopted by the Scientific Committee of the Aerosol Division of the CSMA (Reference 2). The tentative method for determining pickup efficiencies was developed originally to evaluate the efficiencies of residual insecticides as far as deposition on a target was concerned. Although the amount of product that is deposited by a residual insecticide depends upon the particle size, an actual particle size measurement of the products is considered to be impractical and difficult (Reference 3). The pickup efficiency, which is defined as the percentage of the low volatile components that are deposited on a surface, is a function of the particle size and is much easier to determine.

The assumption upon which the present method for comparison of spray properties of aerosol products is based is that within certain limits, different propellants appear to give approximately the same spray characteristics with the same solvent when the propellant/solvent ratios are adjusted so that the pickup efficiencies are the same. The basic assumption includes not only residual aerosol products but also other aerosol products with much finer sprays. As an example, it was determined that mixtures of 72% "Freon - 12"/28% odorless mineral spirits and 87% "Freon - 12"/"Freon - 11" (50/50)/13% odorless mineral spirits both had pickup efficiencies of 60%. Both



mixtures had about the same spray characteristics, judging by visual observation.

The work presented in this report consisted of determining the pickup efficiencies of mixtures of odorless mineral spirits or ethyl alcohol with different propellants. The measurements were carried out with a variety of propellant/solvent ratios and the results were illustrated graphically by plotting the pickup efficiency as a function of the propellant/solvent ratio for each of the propellants. From these graphs, it was possible to determine the propellant/solvent ratios for different propellants that gave the same pickup efficiencies. Propellant/solvent mixtures having compositions that gave the same pickup efficiencies were then prepared and the sprays were compared visually. It was judged, that at the same efficiencies, the spray characteristics of the different mixtures were approximately the same.

Although the data presented in this report were obtained only with propellant/solvent mixtures, the method and data should be applicable to many aerosol products.

Experimental

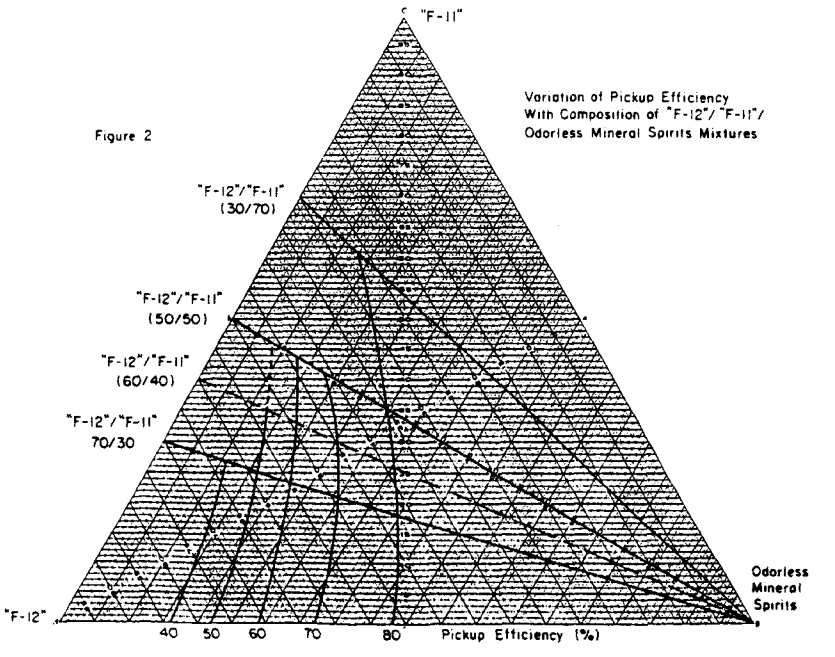
Apparatus and Procedure

The apparatus used for the present experiments was essentially the same as that recommended for the determination of the pickup efficiency of residual insecticides. The construction of the apparatus is described in detail in Reference 2. Basically, it consists of a wooden box with a triple-beam balance mounted on top of the box. A sheet of aluminum, 12" x 12", is suspended inside the box and is attached to the balance by means of a wire which passes through a hole in top of the box. The apparatus is illustrated in the accompanying photographs.

The procedure consists of spraying the aerosol product against a blotter target, clamped to the aluminum sheet, from a distance of one foot. The amount of low volatile material sprayed from the container can be calculated from the weight of aerosol sprayed, assuming that the composition is known. The weight of low volatile material that reaches the blotter target can be determined by the increase in weight of the blotter target. The percent retention on the blotter target of the low volatile material that was sprayed is termed the pickup efficiency. The pickup efficiency is a function of the particle size of the aerosol spray and the smaller the particles the lower will be the pickup efficiency.

In carrying out a pickup efficiency determination, a 12" x 12" piece of ordinary blotting paper was clamped to the aluminum sheet and thus was in a vertical position. A second 12" x 12" piece of blotting paper was placed in a horizontal position at the base so that one edge was in contact with the bottom of the aluminum sheet. The second piece of blotting paper thus extended 12" beyond the aluminum sheet. The aerosol container with the propellant-solvent mixture to be tested was thermostated at 70° F and then placed at the outside edge of the horizontal blotter. The aerosol container therefore was 12" from the vertical blotter clamped to the aluminum sheet.

The aerosol container was sprayed for 10 seconds with the spray directed at the center of the vertical blotter. Particles which were too coarse to



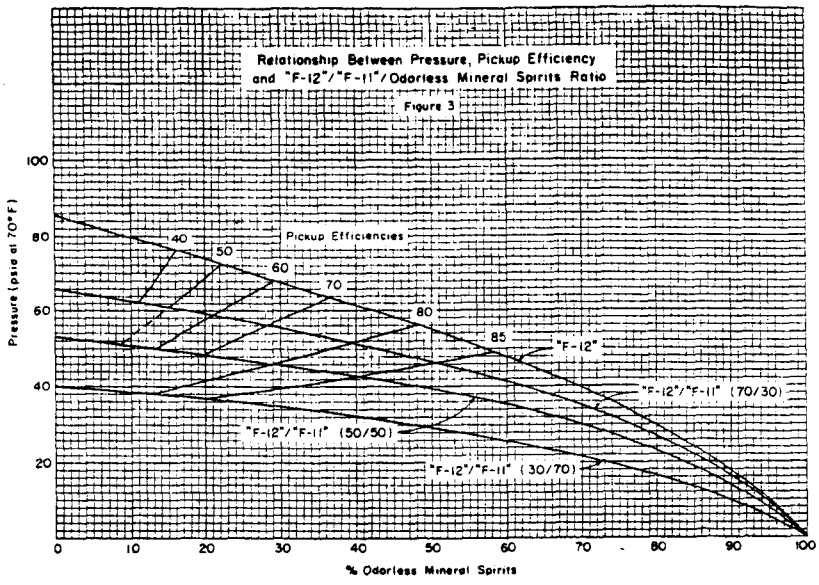
reach the target were caught on the horizontal blotter. Immediately after spraying, the horizontal blotter was folded up against the vertical blotter and clamped. The weight of low volatile material that was deposited on the two blotters was determined using the procedure described in Reference 2. The weight of the blotter targets was determined immediately after spraying and at 3 minute intervals thereafter up to about 15 minutes. The blotters will decrease in weight due to evaporation of both propellant and low volatile solvents. The decrease in weight is plotted as a function of time.

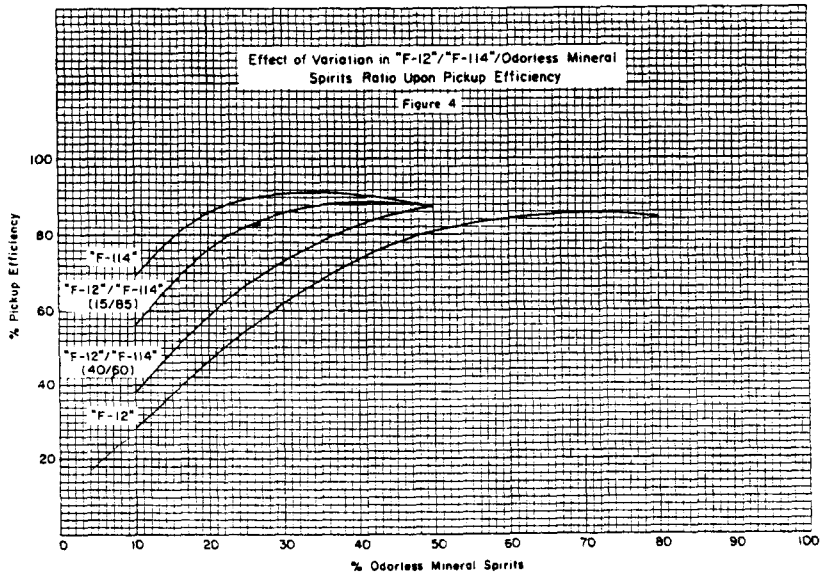
Initially, a rapid decrease in weight occurs which is due mostly to loss of propellant and this is followed by a slower, steady decrease in weight which is due to evaporation of the low volatile solvents. The straight portion of the curve, which represents the evaporation of the low volatiles, is extrapolated back to zero time to give the initial gross weight of the sprayed blotters without including the propellant. From these data, the actual weight of low volatile solvents deposited on the blotter can be determined and the pickup efficiency can be calculated.

All samples were prepared by cold filling in order to keep the air concentration low. At least five determinations were carried out with each propellant/solvent ratio, using different samples for each determination. The results obtained are illustrated graphically in the report, using averages of the separate determinations. The data were obtained with samples packaged with a widely used valve and actuator.

The two solvents used in the tests were odorless mineral spirits and ethyl alcohol. The propellants that were evaluated in combination with the solvents at various propellent/solvent ratios were as follows:

"Freon-12"
"Freon-12"/"Freon-11" (70/30)
"Freon-12"/"Freon-11" (50/70)
"Freon-12"/"Freon-11" (30/70)
"Freon-12"/"Freon-114" (40/60)
"Freon-12"/"Freon-114" (15/85)
"Freon-114"





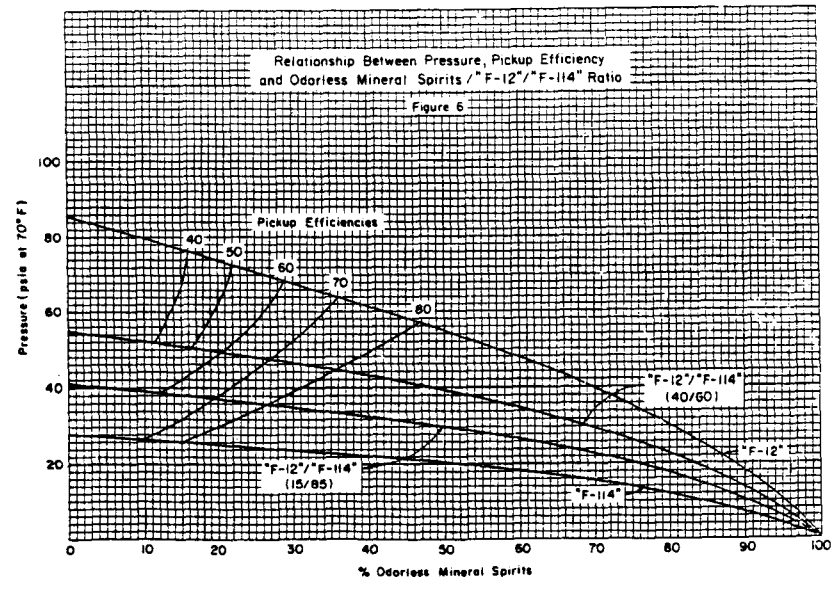


TABLE I

Propellant/Odorless Mineral Spirits Mixtures With Pickup Efficiencies of 70%

Propellant	Propellant/OMS Ratio (wt %)
"Freon-12"	63/37
"Freon-12"/"Freon-11" (70/30)	71/29
"Freon-12"/"Freon-11" (50/50)	81/19

The pickup efficiencies of a variety of propellant/solvent mixtures were determined using the propellants and solvents previously mentioned. The data were first plotted as curves which illustrate the effect of a variation in the propellant/solvent ratio upon pickup efficiency. The data for the various propellant/solvent combinations are illustrated in the following figures:

"Freon-12"/"Freon-11"/Odorless Mineral Spirits ..... Figure 1
"Freon-12"/"Freon-114"/Odorless Mineral Spirits .... Figure 4
"Freon-12"/"Freon-11"/Ethyl Alcohol ..... Figure 7
"Freon-12"/"Freon-114"/Ethyl Alcohol ..... Figure 10

These curves are useful for determining the compositions of various propellant/solvent mixtures that have the same pickup efficiency. Thus, in Figure 1, a dotted line has been drawn through the curves at a pickup efficiency of 70%. From Figure 1 it can be determined that the various propellant/odorless mineral spirits (oms) mixtures that have a pickup efficiency of 70% have the compositions indicated above.

The three propellant odorless mineral spirits mixtures shown in Table I should all have approximately the same spray characteristics if the basic assumption that mixtures with the same pickup efficiencies have the same spray properties is true.

The curves possibly could be extrapolated to zero percent pickup with zero percent solvent present. The curves were not drawn with less than 10% solvent, however, because the variations in pickup efficiency with less than 10% solvent present were too large and the results were not reproducible.

B. Variation of Pickup Efficiency With Composition of Propellant/Solvent Mixtures

The data from Figures 1, 4, 7 and 10 were transferred to triangular coordinate charts to illustrate the variation in pickup efficiency with a variation in the composition of the propellant/solvent blends. The triangular coordinate charts are particularly useful in obtaining the pickup efficiency of propellant/solvent combinations that were not tested experimentally. These data can be obtained by drawing a line from the base line for the particular propellant mixture in question through the solvent apex. For example, the pickup efficiencies of a "Freon-12"/"Freon-11" (60/40) blend with various concentrations of odorless mineral spirits were not determined experimentally but could be obtained from Figure 2 as indicated by the dotted line.

The mixtures that are illustrated on the triangular coordinate charts and the corresponding figure numbers are as follows:

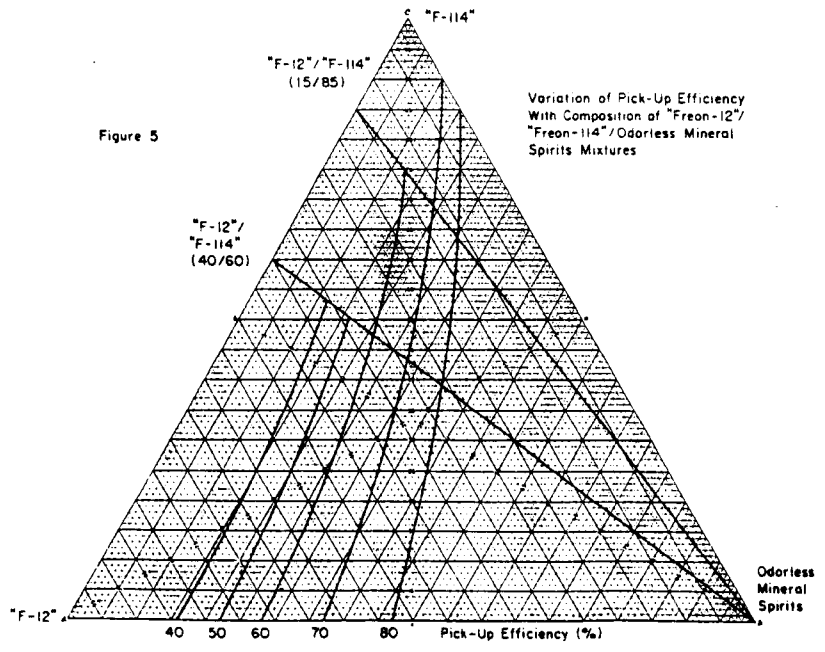
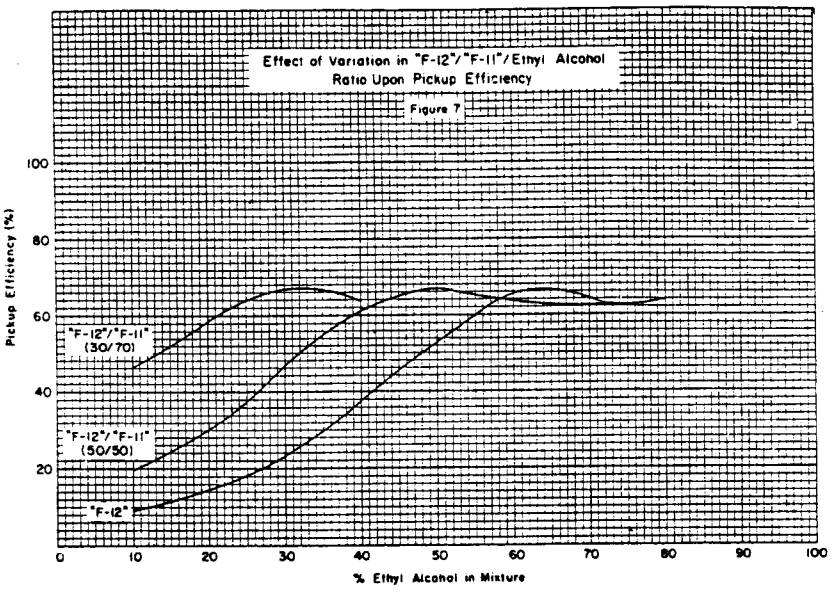


Figure 5 Variation of Pick-Up Efficiency With Composition of "Freon-12"/"Freon-114"/Odorless Mineral Spirits Mixtures

"Freon-12"/"Freon-11"/Odorless Mineral Spirits ..... Figure 2
"Freon-12"/"Freon-114"/Odorless Mineral Spirits ..... Figure 5
"Freon-12"/"Freon-11"/Ethyl Alcohol ..... Figure 8
"Freon-12" "Freon-114"/Ethyl Alcohol ..... Figure 11

C. Relationship Between Pressure, Pickup Efficiency and Propellant/Solvent Ratio

Pressures were determined on a variety of propellant solvent blends so that the relationship between pressure, pickup efficiency and propellant solvent ratio could be established. The samples were prepared by cold filling and pressure measurements were carried out with a prepresurized gage on duplicate samples prepared without dip tubes. The data were plotted with the pressure as a function of the propellant/solvent ratio with the pickup efficiencies shown by contour lines. The various propellant/solvent mixtures and the corresponding figure numbers are as follows:



"Freon-12"/"Freon-11"/Odorless Mineral Spirits ..... Figure 3
"Freon-12"/"Freon-114"/Odorless Mineral Spirits ..... Figure 6
"Freon-12"/"Freon-11"/Ethyl Alcohol ..... Figure 9
"Freon-12"/"Freon-114"/Ethyl Alcohol ..... Figure 12

The data illustrated on these figures make it possible to select a mixture which will give a desired pickup efficiency at a specified pressure.

D. Relationship Between Pickup Efficiencies and Spray Characteristics

In order to check the basic assumption that within certain limits, propellant solvent mixtures with the same pickup efficiencies had about the same spray characteristics, various propellant/odorless mineral spirits and propellant/ethyl alcohol mixtures having the same pickup efficiencies were prepared and the sprays were judged visually.

The results obtained with odorless mineral spirits as the solvent are listed in Table III and the results with ethyl alcohol as the solvent are given in Table II. As a general rule, the propellant odorless mineral spirits mixtures with the same pickup efficiencies had about the same spray characteristics and the same was true with the propellant ethyl alcohol mixtures.

E. Limitations of the Method

As the proportion of propellant in the propellant solvent mixtures is decreased, the sprays become coarser and the pickup efficiency increases until a maximum pickup efficiency is reached. The maximum pickup efficiency obtained with the propellant/odorless mineral spirits combinations was about 85%. That obtained with propellant/ethyl alcohol mixtures was slightly over 60%. Once the maximum pickup efficiency was reached, decreasing the proportion of propellant still altered the spray properties but not the pickup efficiency. Therefore, the method of matching spray properties by using pickup efficiencies is not effective after the maximum pickup efficiency has been reached. Fortunately, this limitation excludes

TABLE II

Relationship Between Spray Characteristics and Pickup Efficiencies—Propellant/Ethyl Alcohol Mixtures

Propellant	Propellant/Ethyl Alcohol Ratio	Pickup Efficiency	Type of Spray
"Freon-12"	73/27	20	Very fine, dry spray
"Freon-12"/"Freon-11" (50/50)	89/11	20	Very fine, dry spray
"Freon-12"/"Freon-114" (40/60)	78/22	20	Very fine, dry spray
"Freon-12"/"Freon-114" (15/85)	86/14	20	Very fine, dry spray
"Freon-12"	59/41	40	Medium to fine
"Freon-12"/"Freon-11" (50/50)	74/26	40	Medium to fine
"Freon-12"/"Freon-114" (40/60)	67/33	40	Medium to fine
"Freon-12"	76/24	40	Medium to fine
"Freon-12"	46/54	60	Medium
"Freon-12"/"Freon-11" (50/50)	61/39	60	Medium
"Freon-12"/"Freon-11" (30/70)	79/21	60	Medium
"Freon-12"/"Freon-114" (40/60)	55/45	60	Medium
"Freon-12"/"Freon-114" (15/85)	66/36	60	Medium
"Freon-114"	79/21	60	Medium

mostly products which have very wet to streamy sprays.

The data in Table IV illustrate the variation in pickup efficiency and spray characteristics with a change in the "Freon-12"/odorless mineral spirits ratio. The maximum pickup efficiency is reached when the "Freon-12" concentration is reduced to about 40%. Decreasing the proportion of "Freon-12" below 40% changes the spray properties but not the pickup efficiency. Similar data obtained with ethyl alcohol as the solvent are shown in Table V. Maximum pickup efficiency was again reached when the "Freon-12" concentration was reduced to about 40% in the mixture.

As previously mentioned, at concentrations of the solvent below 10% in the mixtures, the experimental error in determining the pickup efficiencies was too large for the method to be applicable. The method appears to be useful for formulations in which the solvent concentrations range from about 10% to the point where maximum pickup efficiency is reached. The latter point is a function of the particular propellant and solvent that are used.

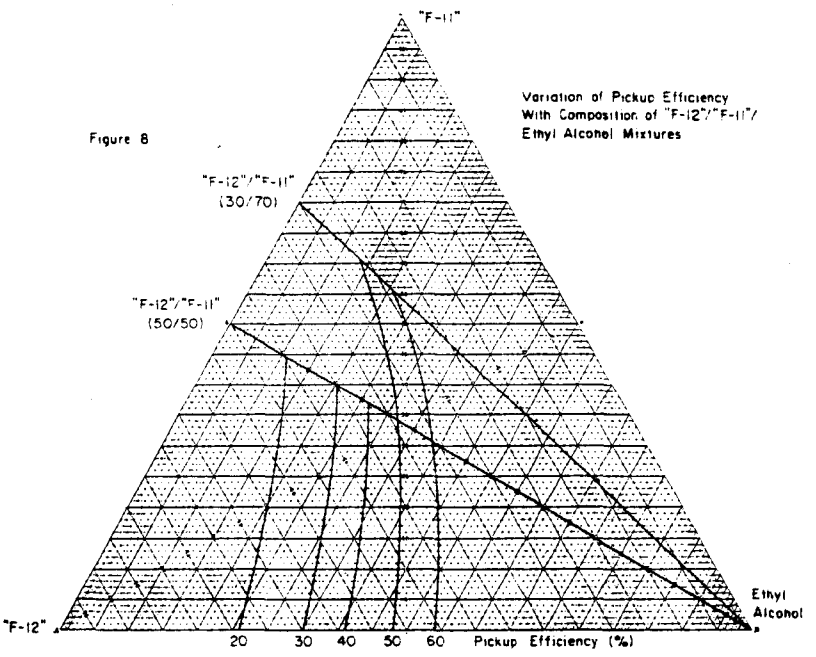
Comments:

The present procedure for matching the spray properties of aerosol products is not intended to be considered as a precise method for indicating compositions having the same particle size distribution. However, the method does appear to indicate the relative proportions of the various propellants which will give sprays with the same general visual appearance.

A limited number of tests were carried out using various valves. As would be expected, the pickup efficiencies were found to be a function of the type of valve used. Therefore, the method can also be used to indicate what effect a variation in valves has upon the spray characteristics of a formulation.

The data in this report were obtained with mixtures of the "Freon" propellants with odorless mineral

Figure 8



Variation of Pickup Efficiency With Composition of "F-12"/"F-11"/ Ethyl Alcohol Mixtures

TABLE III

Relationship Between Spray Characteristics and Pickup Efficiencies—Propellant/Odorless Mineral Spirits Mixtures

Propellant	Propellant/ OMS Ratio	Pickup Efficiency	Type of Spray
"Freon-12"	84/16	40	Very fine
"Freon-12"/"Freon-114" (40/60)	89/11	40	Very fine
"Freon-12"	72/28	60	Fine
"Freon-12"/"Freon-11" (50/50)	87/13	60	Fine
"Freon-12"/"Freon-114" (40/60)	79/21	60	Fine
"Freon-12"/"Freon-114" (15/85)	88/12	60	Fine
"Freon-12"	52/48	80	Medium
"Freon-12"/"Freon-11" (50/50)	72/28	80	Medium
"Freon-12"/"Freon-11" (30/70)	87/13	80	Medium
"Freon-12"/"Freon-114" (40/60)	64/36	80	Medium
"Freon-12"/"Freon-114" (15/85)	75/25	80	Medium
"Freon-114"	85/15	80	Medium

TABLE IV

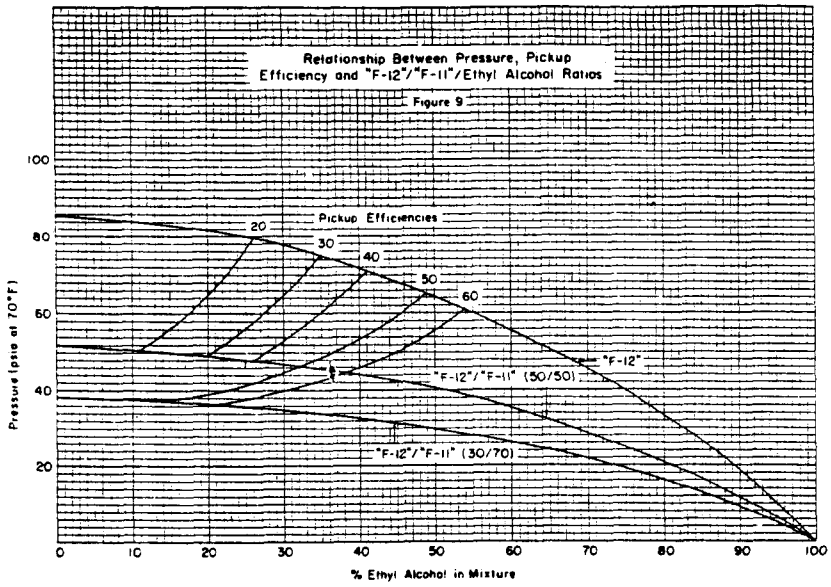
Spray Characteristics and Pickup Efficiencies As a Function of the "Freon-12"/Odorless Mineral Spirits Ratio

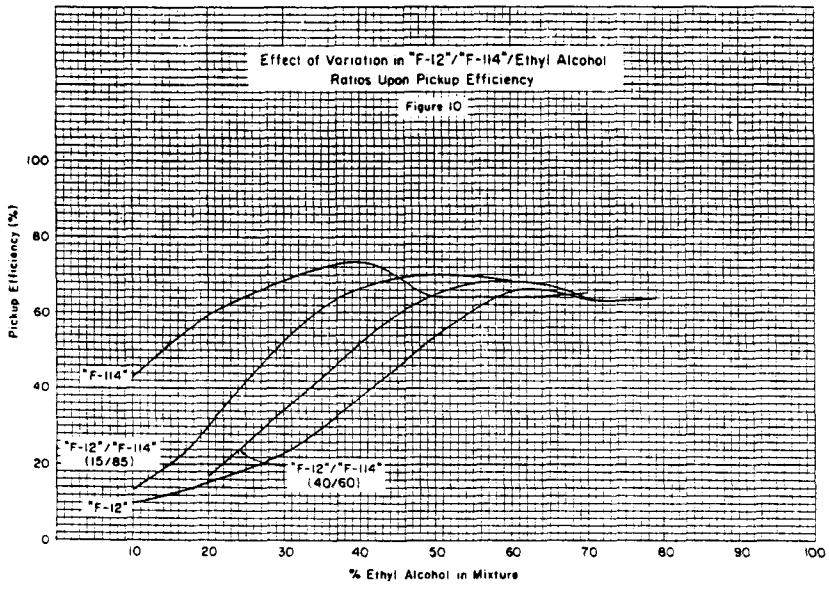
"Freon-12"/ OMS Ratio	Pickup Efficiency	Type of Spray
84/16	40	Very fine
72/28	60	Fine
52/48	80	Medium
40/60	85	Coarse
30/70	85	Broken Stream
20/80	85	Stream

TABLE V

Spray Characteristics and Pickup Efficiencies As a Function of the "Freon-12"/Ethyl Alcohol Ratio

"Freon-12"/Ethyl Alcohol Ratio	Pickup Efficiency	Type of Spray
73/27	20	Very fine
59/41	40	Medium to fine
46/54	60	Medium
40/60	66	Wet
30/70	63	Wet
20/80	64	Partial Stream





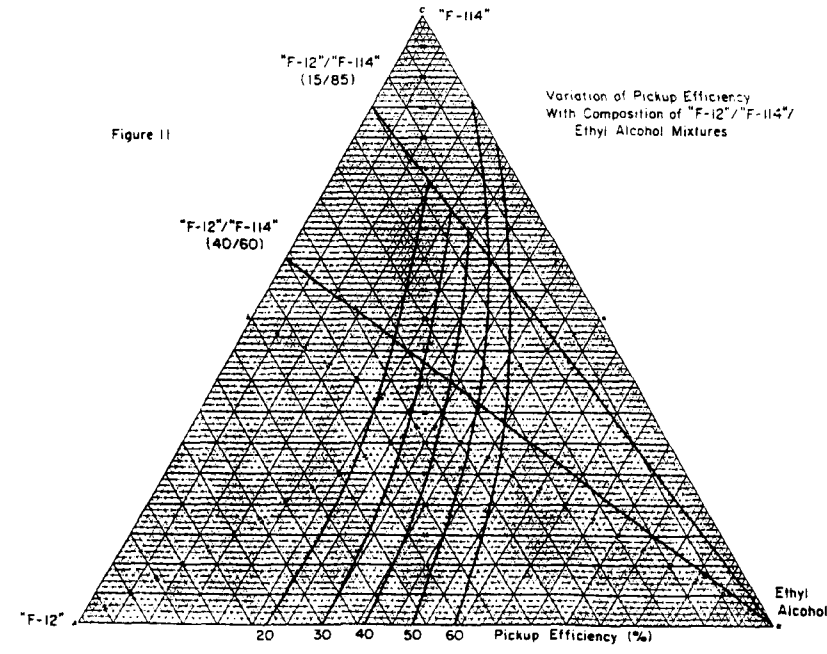


Figure 11

Variation of Pickup Efficiency With Composition of "F-12"/"F-114"/ Ethyl Alcohol Mixtures

spirits and ethyl alcohol. The results should be applicable to most aerosol formulations prepared with these solvents. If similar data are desired for an aerosol concentrate containing other solvents, it might be possible to estimate the pickup efficiencies from the present data by using the boiling points of the solvents in the aerosol concentrates as a guide.

There are other applications in which the determination of pickup efficiencies might be of considerable assistance. For example, the change in spray characteristics of a formulation during complete discharge of the package could be detected by determining the pickup efficiencies of the products at intervals during discharge.

Summary

An empirical method for evaluating the spray characteristics of aerosol products has been developed. The method provides a general indication of the relative proportions of different propellants that will produce the same spray properties. It also shows the effect of varying the propellant concentration upon spray properties. The assumption upon which the method is based is that the spray properties of aerosols formulated with different propellants but the same concentrate, are about the same at the same pickup efficiencies. This assumption appears to be valid within certain limitations.

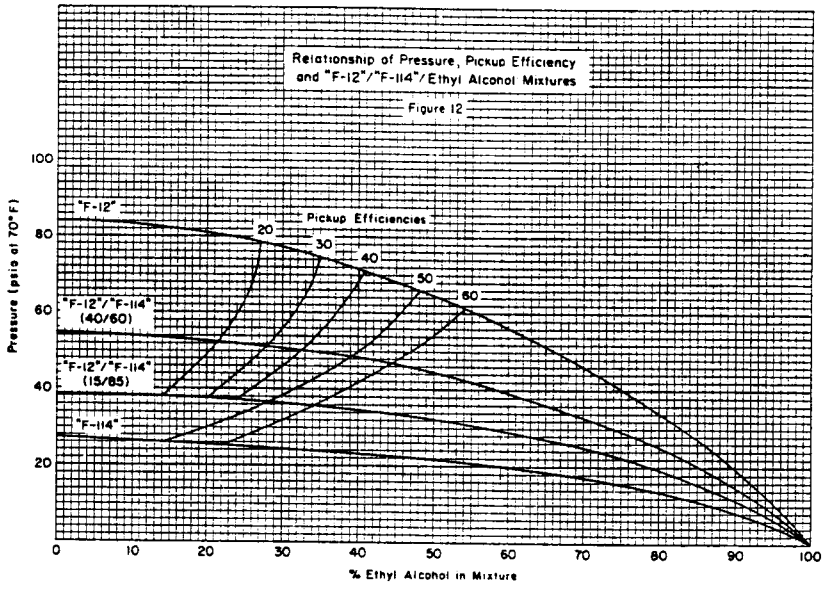
Data are presented for a series of "Freon" propellant/odorless mineral spirits and "Freon" propellant/ethyl alcohol mixtures which illustrate the method of matching and comparing spray characteristics using the pickup efficiency method.

References:

1. "A Tentative Method for Determination of the Particle Size Distribution of Space Insecticide Aerosols", Proceedings of the Forty-third Annual Meeting, CSMA, December 3-5, 1956. ("Freon" Technical Bulletin, A-45).

2. "A Tentative Method for Determining Pickup Efficiency of Residual Aerosol Insecticides", Proceedings of the Forty-third Mid-Year Meeting of the CSMA, May 1957 ("Freon" Technical Bulletin, A-46).

3. Yeomans, A. H., "Particle Size Determinations of Residual Sprays", Proceedings, Fortieth Annual Meeting, CSMA. December 1953.


Relationship of Pressure, Pickup Efficiency and "F-12"/"F-114"/Ethyl Alconol Mixtures
Figure 12
Pressure (psia at 70°F)
100
80
60
40
20
"F-12"
Pickup Efficiencies
20
30
40
50
60
"F-12"/"F-114" (40/60)
"F-12"/"F-114" (15/85)
"F-114"
0
10
20
30
40
50
60
70
80
90
100
% Ethyl Alcohol in Mixture

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