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"FREON" Aerosol Report

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AEROSOL EMULSION SYSTEMS

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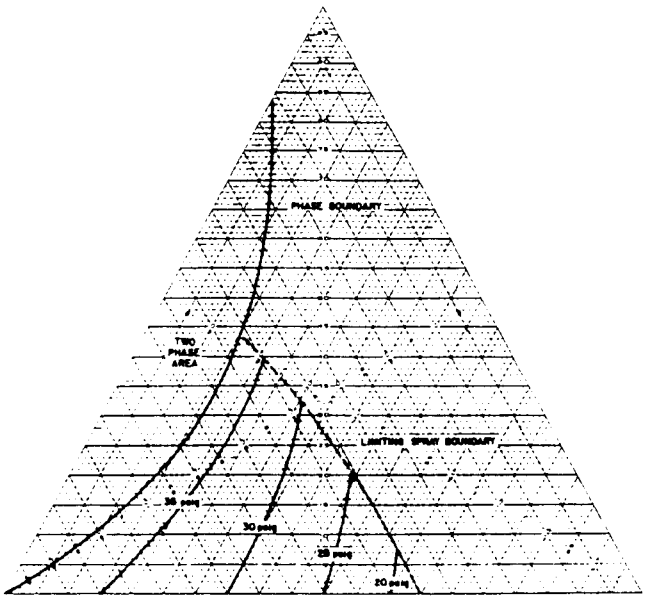

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FREON AND COMPANY DE FREON ... U.S. PATENT AND TRADEMARK OFFICE REGISTERED TRADEMARKS FOR ITS FLUOROCARBON PROPELLENTS

The first aerosol products and the majority of the aerosol products today were formulated as homogeneous systems in which all of the components of the formulation were mutually soluble. In these products the pressure supplied by the propellent forces the solution of active ingredients, solvents and propellent up the standpipe and through the valve. As the solution leaves the valve the liquefied propellent changes into a gas and blasts the solution of active ingredients into fine particles.

There are, however, many materials that would be desirable to spray as aerosols that are soluble in water and have only limited solubility in organic solvents. Water is incompatible with the fluorinated hydrocarbon propellents and the formulation of aqueous-based aerosols giving satisfactory sprays has presented many difficulties. As discussed by Callans (1), the successful formulation of aqueous-based aerosols in the future should lead to a much wider variety of products than are now possible with the homogeneous systems alone and should result in a considerable expansion of the aerosol market.

It is the purpose of this paper to present the various aerosol systems that have been proposed in the attempts to spray aqueous-based products with particular emphasis upon the water-in-oil emulsion systems.

THREE-PHASE SYSTEMS

One of the first successful methods for spraying aqueous systems resulted from the development of the "three-phase" system by Eaton (2) and Mina (3). In this system, the aqueous solution is layered over the denser fluorinated hydrocarbon propellent, which provides the pressure necessary to force the aqueous phase through the standpipe. The latter extends only into the aqueous phase. Since there is essentially no propellent dissolved in the aqueous phase as it passes through the valve, atomization is obtained by the mechanical shearing action of a special valve rather than by flashing of dissolved propellent. At the present time, such valves produce relatively coarse sprays with these systems.

OIL-IN-WATER EMULSION

Aerosol products formulated as oil-in-water emulsions have been on the market since about 1950. These products are the well-known and widely accepted shaving lathers. In these products, a relatively small amount of propellent, usually about 8 to 10 per cent, is emulsified in an aqueous soap solution. As the emulsion is discharged from the foam valve, the propellent expands, forming countless small bubbles. These give the rich lather characteristic of this type of system.

Attempts to obtain fine sprays from such systems by increasing the proportion of propellent and using a spray valve instead of a foam valve result in products which stream. Excessive foaming occurs when the steam impinges on a surface. A series of oil-in-water formulations (4) has been developed that give relatively wet sprays and are essentially nonfoaming. These formulations have low concentrations of propellent, usually less than 5 per cent. By the use of auxiliary solvents, such as ethyl alcohol, almost transparent systems are obtained. These systems have the advantage that no creaming occurs during standing and shaking of the formulation before use is not necessary.

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Window cleaning formulations employing the low propellent oil-in-water system have been marketed for several years and have been well received. These formulations give a soft spray and foam slightly on glass.

WATER-IN-OIL EMULSIONS

During the past several years the Du Pont Company has carried out studies on aqueous-based aerosol systems in an attempt to extend the range of spray characteristics of the water-based aerosol products. This has been found to be possible with the water-in-oil emulsion systems. With such systems, spray properties varying from coarse to very fine may be achieved (5).

It was considered initially that the water-in-oil emulsions should have a fairly good chance of producing nonfoaming sprays. In such systems the water is dispersed throughout the propellent. As the emulsion is forced through the spray actuator, the propellent evaporates, leaving the water droplets, the emulsifying agent, and any auxiliary solvents present. Since very little propellent is dissolved in the aqueous droplets, there is less tendency for the vaporizing propellent to cause foam formation with the droplets. Likewise, since the emulsifying agents suitable for water-in-oil emulsions are generally oil soluble, they are usually poor foaming agents for aqueous solutions.

In choosing the series of emulsifying agents to study, considerable use was made of the list of synthetic detergents assembled by McCutcheon (6). A wide variety of agents were chosen from this list with the selection confined generally to the oil-soluble or known water-in-oil emulsifying agents.

The ultimate selection of the most satisfactory emulsifying agents was based upon the stability of the emulsions, the lack of foaming with the sprays, and the lack of corrosion resulting from the water-in-oil emulsions in metal containers. Of all the agents that were investigated, the polyglycerol esters of the fatty acids were found to be the most satisfactory. Surface-active agents of this type are Emcol 14 (Emulsol Chemical Company) and Soleonic PGE (Sole Chemical Company). Emcol 14, a water-in-oil emulsifying agent, was used exclusively for the preparation of the emulsions described in this paper. In addition to its emulsifying properties, it is reported to be an antifoaming agent (6).

Another effective water-in-oil emulsifying agent for the aerosol systems was Span 20 (sorbitan monolaurate, Atlas Powder Company). This material also is reported to possess antifoaming properties (7).

There are, without doubt, many other surface active agents that would also be effective for preparing aerosol water-in-oil emulsion systems. However, in view of the large variety and number of agents that are commercially available and the time required to evaluate a given agent, it was not possible in the present study to test all materials that conceivably might have been effective.

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EVALUATION OF EMULSION STABILITY AND SPRAY CHARACTERISTICS

The true stability of the emulsion systems as determined by size-frequency analysis was not determined. However, visual observations of the creamed-aqueous phase at various intervals showed that no observable coalesence of the dispersed water drops had occurred with the emulsions that are discussed in the present paper.

Although creaming in an emulsion is not a sign that the emulsion is unstable, it is commercially important because an emulsion that has creamed must be shaken before use. In the present case, rate of creaming is indicated by "separation times." This is the time interval after shaking of the emulsions before visible separation of the two phases occurs. Separation times were determined within one hour after preparation of the emulsions. In many cases it was observed that the separation times for a given series of emulsions changed considerably after the emulsions had aged.

The emulsions were packaged in coated glass bottles for visual observation. The spray characteristics of the emulsions as reported in the tables were determined with a standard glass-bottle valve. In practically all cases, changing from standard actuators to mechanical break-up type of actuators will produce a much finer spray. In many instances, emulsions that stream with the standard actuator will spray with the mechanical break-up type.

"FREON®"* PROPELLENTS STUDIED

The propellents involved in the study were "12" (dichlorodifluoromethane), "114" (dichlorotetrafluoroethane), "11" (trichloromonofluoromethane), and "113" (trichlorotrifluoroethane). Although "11" and "113" are not normally considered as propellents because of their relative low vapor pressures at room temperatures, they will be considered as such in the present paper for ease of discussion.

EXPERIMENTAL RESULTS

Emulsion Stability with the Individual Propellents (17)

The relative stability of water-in-oil emulsions prepared with the individual propellent compounds is as follows, in decreasing order: "11", "113", "12," "114." In Table 1 are listed the separation times for the emulsions prepared with various propellent, water ratios.

The relative stability of the emulsions prepared with the propellent compounds corresponds roughly to the solvent properties of the compounds. This is indicated by a comparison of the Kauri-butanol values (8) for the propellent compounds that are also listed in Table 1. Actually propellent "12" and propellent "114" are such limited solvents that the Emcol 14 used as the emulsifying agent was not sufficiently soluble to form good emulsions.

* *Referred to by number only in remainder of paper.*

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TABLE 1—EMULSION STABILITY OF PROPELLENT-WATER SYSTEMS †

Propellent/Water Ratio, Wt. %	Emulsion Separation Time — Propellent "12"	Propellent "114"	Propellent "11"	Propellent "113"
90/10	<1 min.	<1 min.	15–30 min.	1–5 min.
80/20	<1 min.	<1 min.	15–30 min.	1–5 min.
60/40	<1 min.	<1 min.	>1 hr.	>1 hr.
40/60	1–5 min.	15–30 min.	>1 hr.	>1 hr.
Kauri-Butanol values of propellents	18	11.8	60.1	32

† 4 parts of Emcol 14/104 parts of emulsion.

PROPELLENT-WATER EMULSIONS

Satisfactory water-in-oil emulsions with "12"/"114" solutions or "114" alone as the propellent have not yet been achieved. As previously mentioned, these two propellents have limited solvent properties and the surface active agents in general were not sufficiently soluble in the propellents to form stable emulsions.

Propellents "12"/"11"/Water Emulsions

Fairly satisfactory emulsions may be obtained by combining "11", with its relatively good solvent powers, with "12." The spray characteristics of the emulsions may be varied from very fine to very wet by varying either the "12"/"11" ratio or the propellent/water ratio.

The effect of varying the "12"/"11" ratio upon spray characteristics and emulsion separation times is shown in Table 2. The variations were tested at propellent/water ratios of 80/20 and 60/40, respectively. As the data in Table 2

TABLE 2—EFFECT OF VARIATION IN PROPELLENT "12"/PROPELLENT "11" RATIO UPON EMULSION AND SPRAY PROPERTIES

Propellent 12"/11" Ratio, Wt. %	Separation Times	Spray Characteristics	Propellent 12"/11" Ratio, Wt. %	Separation Times	Spray Characteristics
80/20 Propellent/Water Ratio			60/40 Propellent/Water Ratio		
100/0	<1 min.	...	100/0	<1 min.	...
70/30	<1 min.	Very fine	70/30	30–60 min.	Fine
50/50	1–5 min.	Fine	50/50	30–60 min.	Medium fine
30/70	15–30 min.	Medium fine	30/70	30–60 min.	Soft medium
0/100	15–30 min.	No spray	0/100	>1 hr.	No spray

4 parts Emcol 14/104 parts final emulsion

indicate, increasing the proportion of "11" in the propellent mixture increases the stability of the emulsions and also the wetness of the spray. Both of these effects would be predicted on the basis of the data in Table 1 and the fact that "11" lowers the vapors pressure of "12," thus giving propellent mixtures that produce coarser sprays.

EID11613

The effect of varying the propellent/water ratio upon emulsion stability and spray characteristics is given in Table 3. In these experiments the "12"/"11" ratio was held constant at 30/70.

TABLE 3—EFFECT OF VARIATIONS IN PROPELLENT* WATER RATIO UPON CREAMING AND SPRAY CHARACTERISTICS

Propellent/Water Ratio, Wt. %	Separation Times	Spray Characteristics
90/10	1–5 min.	Very fine
80/20	5–15 min.	Fine
60/40	30–60 min.	Medium
40/60	>1 hr.	Very coarse—almost foams
20/80	<1 min.	Stream—foams

Emulsions prepared with 4 parts Emcol 14/104 parts of finished emulsion

* Propellent is "12"/"11" (30/70).

In this series, increased emulsion stability and increased wetness of sprays result with a decrease in the propellent/water ratio. The increase in stability probably results primarily from the increase in viscosity of the emulsions that occurs as the proportion of water is increased. This point will be discussed in more detail later.

Emulsions of "12"/"11" generally exhibit slight bubbling when sprayed on a surface. For some uses, this may be undesirable. The bubbling probably results from vaporization of the "11" that is retained in the spray.

Emulsions with Auxiliary Solvents

The use of auxiliary solvents, such as odorless mineral spirits, has a number of advantages in formulating aerosol water-in-oil emulsions. As shown later, the solvents may increase emulsion stability, particularly with emulsions formulated with "12" alone or "12"/"114" solutions as the propellents.

As previously noted, "12"/"11" water emulsions tend to cause bubbling when sprayed on a surface. The addition of an auxiliary solvent may minimize or eliminate the bubbling entirely.

The ease of preparation of the emulsions is increased considerably by the use of solvents. For example, the solvent may be used to dissolve the water-insoluble surface-active agent. A water-in-oil emulsion is then prepared from the solvent by adding the water to the solvent. This emulsion is used to fill the aerosol container. The propellent is pressure loaded after capping the container. In this case, the addition of propellent to the previously formed emulsion can be considered merely as extending the continuous oil phase.

Under the present ICC regulations, "12"/water emulsions would not be permissible in the standard aerosol containers as a result of pressure limitations. Auxiliary solvents serve as pressure depressants for "12" and permit the formulation of emulsions using "12" alone as the propellent.

EID11614

Propellent "12"/Solvent/Water Systems

Emulsion systems of "12"/odorless mineral spirits/water produce nonfoaming sprays. The spray characteristics themselves may be varied over a wide range from very fine to very coarse by changing the "12"/solvent ratio. Examples of this are listed in Table 4.

TABLE 4—PROPELLENT "12"/ODORLESS MINERAL SPIRITS/WATER EMULSIONS

Propellent "12"/OMS* H_2O Ratio, Wt. %	Separation Times Without "12"	Separation Times With "12"	Spray Characteristics
60/20/20	>1 hr.	1–5 min.	Fine
40/20/40	>1 hr.	>1 hr.	Medium
20/20/60	>1 hr.	>1 hr.	Wet
60/30/10	5–15 min.	1–5 min.	Fine
60/10/30	>1 hr.	1–5 min.	Fine

4 parts Emcol 14/104 parts of finished emulsion

* OMS = Odorless mineral spirits.

As discussed previously, "12"/water emulsions of satisfactory stability were not obtained. As shown by the data in Table 4, the effect of the odorless mineral spirits is to increase the emulsion stability considerably. A comparison of the stability of the odorless mineral spirits/water emulsions before and after the addition of "12" is also shown in order to indicate the effect of the "12" upon the emulsion stability. Propellent "12" decreases the emulsion stability but in most cases the stability is still sufficient for practical purposes.

Odorless mineral spirits is one of the best solvents for obtaining nonfoaming sprays. For certain applications, other solvents such as cottonseed oil may be more desirable. These solvents form fairly good emulsions but in some cases there appears to be a tendency to promote slight bubbling or foaming.

Propellent "12"/"114"/Odorless Mineral Spirits/Water Emulsions

Pressure of 25 psig. or less at 70°F, are generally considered desirable for aerosols to be packaged in glass. In "12" odorless mineral spirits/water systems pressures below 25 psig may be achieved by the proper ratio of propellent to solvent. As discussed later, however, the extent to which this can be done is limited by flammability considerations. In order to obtain pressures below 25 psig. it may be necessary to have such a low propellent/solvent ratio that the product is flammable. It is also found that emulsions with sufficiently low "12"/odorless mineral spirits ratios to satisfy the pressure requirements generally give excessively wet sprays.

The above difficulties may be eliminated by formulating with "12"/"114" solutions as the propellent. Emulsion systems producing sprays ranging from very wet to fine may be obtained by varying the ratio of "12" to "114." The propellent solutions with a low concentration of "12," that would be satisfactory for glass bottle aerosols, give very soft sprays.

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TABLE 5—PROPELLENTS "12"/"114"/ODORLESS MINERAL SPIRITS/WATER EMULSION

Propellents "12"/"114" Ratio, Wt. %	Separation Times	Spray Characteristics	Propellents "12"/"114" Ratio, Wt. %	Separation Times	Spray Characteristics
Propellent/Solvent/Water Ratio—60/20/20			*Propellent/Solvent/Water Ratio—40/20/40*		
0/100	1–5 min.	Soft—medium wet	0/100	15–30 min.	Very wet
15/85	1–5 min.	Soft—medium wet	15/85	15–30 min.	Medium wet
40/60	1–5 min.	Medium	40/60	15–30 min.	Medium
57/43	1–5 min.	Medium fine	57/43	>1 hr.	Medium
100/0	1–5 min.	Fine	100/0	>1 hr.	Medium fine

2 parts Emcol 14/102 parts finished emulsion

The effect of varying the "12"/"114" ratio upon emulsion stability and spray characteristics is indicated by the data in Table 5. Data were obtained for propellent/solvent/water ratios of 60/20/20 and 40/20/40.

Propellent "12"/Propellent "11"/Solvent/Water Emulsions

The "12"/"11"/odorless mineral spirits/water combinations provide nonfoaming sprays with relatively good emulsion stability. As in the previous case with the "12"/"11"/water emulsions, the spray characteristics of the present type may be varied considerably by varying the ratio of "12" to "11." Spray characteristics and separation times of a series of this type are given in Table 6.

At a given "12"/"11" ratio, the spray characteristics of the emulsion may be varied by varying the concentration of the propellent. This appears to have a greater effect than keeping the concentration of the propellent constant and varying the solvent/water ratio. Data for a series of "12"/"11" (30/70)/odorless minerals spirits/emulsions are given in Table 7.

TABLE 6—PROPELLENTS "12"/"11"/ODORLESS MINERAL SPIRITS/WATER EMULSION

Propellents "12"/"11" Ratio, Wt. %	Separation Times, Min.	Spray Characteristics
Propellent/Solvent/Water Ratio—60/20/20		
100/0	1–5	Fine
70/30	30–60	Medium fine
50/50	30–60	Medium
30/70	30–60	Wet
0/100	...	Stream

2 parts Emcol 14/102 parts finished emulsion

TABLE 7—PROPELLENTS "12"/"11" (30/70)/ODORLESS MINERAL SPIRITS/WATER EMULSIONS

Propellent/Solvent/Water Ratio	Separation Time, Min.	Spray Characteristics
60/10/30	30–60	Medium wet
60/15/25	30–60	Medium wet
60/20/20	30–60	Medium wet
40/20/40	30–60	Partial stream
20/20/60	...	Stream
60/30/10	30–60	Medium wet
40/30/30	30–60	Stream
50/40/10	30–60	Stream

2 parts Emcol 14/102 parts finished emulsion

EID11616

Effect of Ethyl Alcohol upon Emulsion Stability.

The water-in-oil emulsion systems can tolerate a fairly high concentration of alcohol in the aqueous phase without an appreciable effect upon emulsion creaming time. The effect of the alcohol was determined with "12" "11" (30 70) odorless mineral spirits water systems emulsified with Emcol 14. Concentrations of ethyl alcohol in the aqueous phase up to 30 per cent had no effect upon emulsion stability. Higher concentrations, however, caused a definite decrease in emulsion stability.

Effect of Sodium Chloride upon Emulsion Stability

The effect of sodium chloride in the aqueous phase at concentrations of 10 and 25 per cent was evaluated in various emulsion systems containing odorless mineral spirits as the auxiliary solvent. The emulsion creaming time was decreased in all cases, although it was still sufficient for most purposes.

The emulsions containing the sodium chloride were considerably less milky than the corresponding emulsions without sodium chloride. The sodium chloride appeared to affect the ease of dispersion of the water rather than the strength of the interfacial film. The creamed aqueous layers appeared visually, at least, to be stable without an observable coalescence of water drops.

Viscosity of the Water-in-Oil Emulsions and Phase Changes

The viscosity of the water-in-oil emulsions is a function of the concentration and type of auxiliary solvents, concentration of propellents, aqueous phase, and emulsifying agent. As would be expected, the viscosity of the emulsions increases as the portion of the dispersed aqueous phase increases. Electrical conductivity measurements indicate the emulsions to be of the water-in-oil type. Likewise, creaming occurs from the bottom as would be expected with a water-in-oil emulsion where the dispersed aqueous phase is less dense than the continuous phase and rises to the top. Essentially no foaming occurs when the bottles are shaken. As the viscosity of the emulsions increases the separation times become greater as a result of the increased difficulty of movement of the dispersed water droplets.

As the concentration of the aqueous phase is increased to 60-80 per cent, inversion of the emulsion from water-in-oil to oil-in-water generally occurs. After inversion the viscosity of the emulsions decreases with a corresponding decrease in separation time. Electrical conductivity measurements indicate the emulsions to be of the oil-in-water type and creaming now occurs from the top with the denser dispersed propellent phase settling to the bottom.

The oil-in-water emulsions foam considerably when shaken, in contrast to the water-in-oil emulsions. Where the previous water-in-oil emulsions gave a nonfoaming spray, the oil-in-water emulsions produce a stream that foams on contact.

These results appear to be similar to those obtained by Sherman (9), who noted that the viscosities of water-in-oil emulsions prepared with distilled water in mineral oil reached a maximum value between 77 and 82 per cent water. At higher concentrations of water, inversion of the emulsion occurred. The concentration at which inversion occurred was a function of the amount of emulsifying agent present.

EID11617

Occasionally it was observed that of two supposedly duplicate samples prepared with 20 per cent propellent and 80 per cent water, one was a very viscous water-in-oil emulsion while the other sample was the less viscous oil-in-water type. The separation time of the former was generally greater than an hour with creaming occurring from the bottom while the separation time of the latter was less than a minute with creaming occurring from the top. This was probably a case of the formation of dual emulsions emulsions with the same liquids and emulsifying agents but having opposite phase types (10), where the type of emulsion that was obtained depended upon how the bottle was shaken. This phenomenon, where the phase type of the emulsion is determined by the type of agitation, was first observed by Ostwald (11) and later confirmed by Cheesman and King (12).

The electrical conductivity of the emulsions was found generally to be a reliable means for determining the phase of the propellent water emulsions. In most of the cases investigated the water-in-oil emulsions were essentially nonconducting as the inversion point was approached and became conducting after inversion had occurred. However, with "12"/"11" (30/70)/water emulsions, it was observed that the emulsion containing 40 per cent propellent and 60 per cent water exhibited an electrical conductance intermediate between that of the nonconducting emulsions with 60 per cent propellent 40 per cent water and the conducting 20/80 emulsion. It is possible that in cases of this type, application of the electric current caused partial inversion of the water-in-oil emulsion to take place. This effect with water-in-oil systems has been reported by Dixon and Bennet-Clark (13).

Particle Size of Emulsion Sprays

At the present time, very little information on the particle size of the emulsion sprays is available. Attempts to determine the particle size of the emulsions at the "Freon" Products Laboratory by the standard technique involving the rotating slide and wind tunnel (14) have not been successful as yet. In the cases studied, the water evaporated before the droplets reached the slide.

In the water-in-oil propellent/water emulsions, the particle size of the sprays is probably controlled to a considerable extent by the degree of dispersion of the water droplets in the propellent. If this is true, the particle size from a given formulation will depend upon the method and efficiency of emulsification.

An additional factor probably should be considered and that is the effect upon the emulsion stability resulting from the passage of the emulsion through a valve. In the emulsions containing a high proportion of water, the droplets are close together. It appears likely that during the violent agitation occurring in the emulsions during the passage through the valve and immediately following their exit from the outer orifice, considerably more coalescence of the water droplets would occur with the concentrated emulsions than with the dilute emulsions. If this happens, then the particle size of the sprays from the concentrated emulsions will be much larger than those from the dilute emulsions regardless of the fact that the size of the dispersed water droplets was the same in both emulsions before spraying.

EID11618

The picture becomes even more complicated in emulsions formulated with an auxiliary solvent, such as odorless mineral spirits. In this case the propellent is dissolved in the solvent and the flashing of the propellent during spraying breaks the solvent into fine particles. The particle size of the sprayed solvent will depend therefore upon the ratio of propellent to solvent, as in any homogeneous system. What effect the break-up of the solvent has upon the dispersed water droplets is not known. It is possible that the auxiliary solvent and water are sprayed as separate droplets. However, if this occurs, then re-emulsification occurs, when the two phases impinge upon a surface. Experiments show that an emulsion is obtained when a propellent, solvent, water emulsion is sprayed into a container.

Corrosion Studies with Water-in-Oil Emulsions

The combination of water and surface-active agents in aerosol systems always introduces the possibility of corrosion of metal containers. The difficulties that have been encountered in attempts to package aerosol shampoos based on fatty alcohol sulfates are well known. On the other hand, aerosol shave lathers based on fatty acid soaps have an excellent record with respect to corrosion.

The basic water-in-oil emulsion systems discussed in the present report appear generally to have remarkable stability as far as corrosion of metal containers is concerned. The emulsions were packaged in the following containers for the specified storage temperatures and times:

1. Crown lacquer-lined tin-plate cans equipped with Precision nylon-brass valves
   Aging periods: 2 months at 130°F
   1 year at room temperature

2. Continental tin-plate cans equipped with Precision nylon-brass valves
   Aging periods: 6 months at 100°F
   1 year at room temperature

The particular emulsion systems that were evaluated were as follows:

1. Propellent "12" deodorized kerosene/water–60/20/20 ratio
2. Propellents "12" "114" (15/85)/"Nujol"/water–60/20/20 ratio
3. Propellents "12" "11" (30/70)/"Nujol"/water–60/20/20 ratio
4. Propellents "12" "11" (30/70)/water–80/20 and 60/40 ratios

The first three emulsions systems produced no observable corrosion in any of the containers under any of the storage conditions. The fourth system, "12"/"11"/water emulsions, caused no corrosion in the lacquer-lined containers under any of the storage conditions nor did they cause corrosion in the tin-plate containers at room temperature. After six months of 100°F, however, slight detinning on the can shoulders was observed.

The general lack of corrosion observed with the emulsion systems is encouraging. It should be recognized, however, that the addition of active ingredients may introduce corrosive characteristics into the system. It is necessary, therefore, to shelf test any practical formulations.

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It has been proposed by Boe (15) that the water-in-oil systems would be expected to show less corrosion than the oil-in-water systems because in the former, the dispersed water has less tendency to come into contact with the container and valve. This may well be an important factor. On the other hand, the surface-active agent that is used also has an important bearing upon the corrosion that is observed. Some of the other water-in-oil emulsions prepared with agents other than the Emcol 14 were found to cause considerable corrosion.

Pressures of Aerosol Formulations

The pressures resulting with the propellent/solvent/water emulsions are substantially those of the propellent/solvent mixture. The pressures of such mixtures will depend upon the ratio of the mixtures and the particular propellent and solvent that are used. Examples of the pressures of such mixtures are given in Reference 5 and need not be considered in more detail here. In cases where the proportion of propellent is low and the relative proportion of oil-soluble emulsifying agent is high, then the emulsifying agent will contribute to a lowering of the vapor pressure of the propellent.

Flammability

These propellents are nonflammable. As a result, all of the propellent/water emulsions are also nonflammable. However, when a flammable auxiliary solvent, such as odorless mineral spirits, is used in the formulation then the flammability properties must be determined.

The flammability characteristics of a series of emulsions with varying concentrations of odorless mineral spirits are given in Tables 8 and 9. The propellents were "12" and "12"/"11" (30/70), respectively. The flammability characteristics were evaluated by the flame extension and the flame sustaining tests.

The flammability of the formulations appears to be a function of the concentration of auxiliary solvent, concentration of water, and spray characteristics. The data in Table 8, for example, indicate that emulsions with 20 per cent odorless mineral spirits are nonflammable, those with 30 per cent are flammable but do not sustain a flame, and those with 40 per cent are flammable and sustain a flame.

The ratio of propellent to solvent does not appear to be a controlling factor. Thus, as shown in Table 8, "12"/odorless mineral spirits water emulsions with 40/20/40 ratios were nonflammable whereas those with a 60/30/10 ratio were flammable. In both cases the propellent/solvent ratio is the same. This is also shown in Table 9 where the "12"/"11" (30/70) odorless mineral spirits water emulsion with the composition ratio of 60/20/20 was flammable but the emulsion with the lower propellent/solvent ratio of 40/20/40 was nonflammable.

The spray characteristics appear to play a role in determining the flammability of the product. In Table 9, the "12"/"11" (30/70) odorless mineral spirits/water emulsion with the composition ratio of 50/40/10 was nonflammable in spite of the high concentration of solvent. This product had a very wet spray with the standard actuator. On the other hand, the emulsion with a 60/30/10 ratio was flammable with the lesser concentration of solvent.

EID11620

Changing the valve actuator from a standard actuator to a mechanical break-up type in some cases may shift a product that is flammable by the flame extension test into the nonflammable class by widening the angle of spray. This may also convert a product that does not sustain a flame into one that does, probably by better aeration of the sprayed material.

TABLE 8—FLAMMABILITY OF PROPELLENT "12"/ODORLESS MINERAL SPIRITS/WATER EMULSIONS

Propellent/ OMS/Water Ratio	Flammability			
	Standard Actuator		Mechanical Break-up	
	Flame Ext.	Flame Sust.	Flame Ext.	Flame Sust.
60/20/20	NF*	NF	NF	NF
40/20/40	NF	NF	NF	NF
20/20/60	NF	NF	NF	NF
60/30/10	FL	NF	NF	FL
40/30/30	FL	NF	NF	FL
20/30/50	FL	NF	NF	NF
50/40/10	FL	FL	FL	FL
40/40/20	FL	FL	NF	FL
20/40/40	FL	NF	NF	FL

2 parts Emcol 14/102 parts emulsion

* NF, nonflammable; FL, flammable.

TABLE 9—FLAMMABILITY OF PROPELLENTS "12"/"11" (30/70), ODORLESS MINERAL SPIRITS/WATER EMULSIONS

Propellent/ OMS/Water Ratio	Flammability			
	Standard Actuator		Mechanical Break-up	
	Flame Ext.	Flame Sust.	Flame Ext.	Flame Sust.
60/15/25	NF*	NF	NF	NF
60/20/20	FL	NF	NF	NF
40/20/40	NF	NF	NF	NF
60/30/10	FL	FL	NF	NF
40/30/30	NF—Stream	NF	NF	NF
50/40/10	NF—Very wet	NF	NF	NF
40/40/20	NF—Stream	NF	NF	NF

2 parts Emcol 14/102 parts emulsion

* NF, nonflammable; FL, flammable.

Potential Applications of the Water-in-Oil Emulsions

The water-in-oil emulsion systems that have been presented are obviously basic formulations. By the addition of suitable active ingredients, formulations with practical applications will be developed. The active ingredients do not necessarily have to be soluble in the aqueous phase. Organic soluble materials can be dissolved in the auxiliary solvent and water alone added if an emulsion type is desired. Also, organic soluble and water-soluble active ingredients can be combined in the same formulation by dissolving the former in the auxiliary solvent and the latter in the aqueous phase.

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As discussed in the previous sections, the spray characteristics of the emulsion systems can be varied from very fine to very wet by suitable choice of the emulsion system. This wide range of available spray characteristics provides a variety of potential applications from topical products, such as antiseptics, antiperspirants, etc., where a wet spray is desired, to room deodorant and sanitizer sprays, where a fine mist is necessary.

In formulating, factors such as the type of container to be used, the pressure of the systems, type of spray, flammability, emulsion stability, and corrosion must all be considered. For many products, such as sun tan sprays, a water-in-oil emulsion system with an auxiliary solvent is particularly desirable since it adheres to the skin and is not readily removed by water. In other cases, where contact of the aqueous phase with the skin is desired, a high boiling organic solvent is not desirable and an emulsion prepared without an auxiliary solvent or with a lower boiling auxiliary solvent, such as propellent "113" would be preferred.

Most of the emulsion sprays, particularly those with axuiliary solvents, do not have an undersirable chilling effect on the skin. This is a considerable advantage for topical applications.

In most cases, redispersion of the creamed aqueous layer occurs with ease. In some cases, particularly where the viscosity of the emulsion is high, redispersion takes place in the aerosol container but not in the standpipe. When this occurs, the initial spray consists of an aqueous stream followed by the normal spray. This is undersirable and it is generally necessary to reformulate the product. Of course, if the container is used in an inverted position without a standpipe, the problem does not exist.

EXPERIMENTAL

Preparation of Emulsions

The method of preparation of the various emulsions depended upon the particular propellent and system involved. Water emulsions of "11" or "113" were prepared by dissolving the surface-active agent in this propellent compound, adding the water, and shaking to form the emulsion. As "12" and "114" are gases at room temperature, they must be handled differently. Emulsions of either of the above with water were prepared either by dispersing the agent in the water and pressure loading the propellent solution of the agent. The latter is the preferred procedure.

Many of the emulsions were formulated with an auxiliary solvent, such as odorless mineral spirits. In such cases, the surface active agent was dissolved in the solvent and the aqueous phase added slowly with agitation. The resulting water-in-oil emulsion was then poured into a coated bottle. If "11" or "113" were used in the formulation, they were added at this time and the bottle was capped. The remainder of the propellent was pressure loaded.

After loading was completed, the emulsions were shaken 20 times by hand to complete the dispersion and the separation times were determined within an hour after pressure loading the propellent.

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Determination of Emulsion Type

Determination of emulsion type was generally carried out with the electrical conductivity apparatus described by Griffin (16). For emulsions under pressure the apparatus was modified by fitting the electric contacts into a glass pressure-tube as discussed in Reference 5.

SUMMARY

The various methods available for spraying water-based aerosol products are reviewed with emphasis upon the water-in-oil emulsion systems. By suitable choice of propellents and auxiliary solvents, nonfoaming sprays varying from very fine to very coarse may be obtained. The characteristics and properties of the emulsion systems, such as emulsion stability, flammability, viscosity, stability to electrolytes and alcohol, and particle size of the sprays are discussed.

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(17) Fluorinated hydrocarbon propellents used in the preparation of this paper are manufactured under the trade name "Freon" by E. I. du Pont de Nemours and Company, Inc. of Wilmington, Delaware.

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