Procedures to Guide Experiments Directed to Improvement of Electrostatic Atomization and Deposition of Organic Coatings

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Synopsis

Methods are described for determination of particle size D of paint atomized in an electrostatic field and for measurement of band width B and wraparound ratio W of a film pattern produced under standard conditions. A quantitative "figure of merit" F, defined as the ratio BW/D, can be correlated with qualitative aberrations of electrospray efficiency. This quantitative measure provides a more efficient guide to experiments directed toward upgrading electrospray performance of otherwise useful paints. Some examples are cited to demonstrate that incorporation of highly charged colloidal particles have significant effects on electrospray efficiency of paints containing vehicles of low conductivity.

In pure electrostatic spray painting, high voltage fields cause paints to be atomized into extremely fine particles that carry a charge. The charged particles are attracted to the oppositely charged workpiece and deposited on the substrate under the action of the electrostatic field. The apparatus used to accomplish this result basically consists of a method of presenting the fluid coating material in the form of a thin, extended film at a sharpened edge of a supporting member where it is exposed to the electric field. In commercial practice such apparatus takes the form of a rotating bell-shaped head or disk. The coating material is fed to the inside surface of the bell or the exposed surface of the disk. Rotation of the bell or disk levels the coating material into a thin film and causes it to flow toward the mouth of the bell or the edge of the disk. At this point the high gradient of the electric field at the edge takes over and forms the film edge into a series of closely spaced cusps. From the tips of these cusps the small charged particles of coating material are atomized (Fig. 1). Under the action of the field, they are dispersed, carried to the oppositely placed article, and precipitated on its surface.

In the case of the bell-type atomizer, the atomized paint leaving the annular edge of the bell forms on an oppositely disposed flat surface an annular, doughnut-shaped pattern (see Fig. 6). With the disk the material leaves the entire circumference of the unit in the form of an expanding spray. To use all the spray effectively, therefore, articles are carried about a full loop surrounding the disk in spaced relationship to its edge.

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Fig. 1. Contact print (without enlargement) showing cusps and atomization near edge of 4 in. bell at 900 rpm, delivery rate of paint 100 cc./min., 100 kv.; good atomization (fine particle size).

With these arrangements practically all the atomized coating material leaving the disk or bell is deposited on the articles. Coating efficiency is essentially 100%. This is a great improvement over the widely used air spray gun which at best has a coating efficiency of about 50%. This savings potential of electrostatic methods has led to their being widely adopted in industry. Their use in turn creates the interest and motivation for further studying the mechanism of the process and how coating material characteristics influence their behavior in these processes.

Atomization, transportation, collection, discharge, and coalescence of particles, followed by spreading of the wet paint film on the target, are separate events of the process system of electrostatic spraying of paint, each of which is governed by a different combination of variables and each of which may be influenced in a peculiar way by the field.

Since different coating materials vary greatly in composition, and since the different components of these materials each may have varying effects on one or more of the several events of the spray and film-forming process, it is not surprising that they respond to the electrostatic process with a wide variety of behaviors. Variations in the viscosity of the liquid material, its evaporation rate, its basic resin composition, its solvent composition, its electrical conductivity, dielectric constant, its electrical polarity, all are
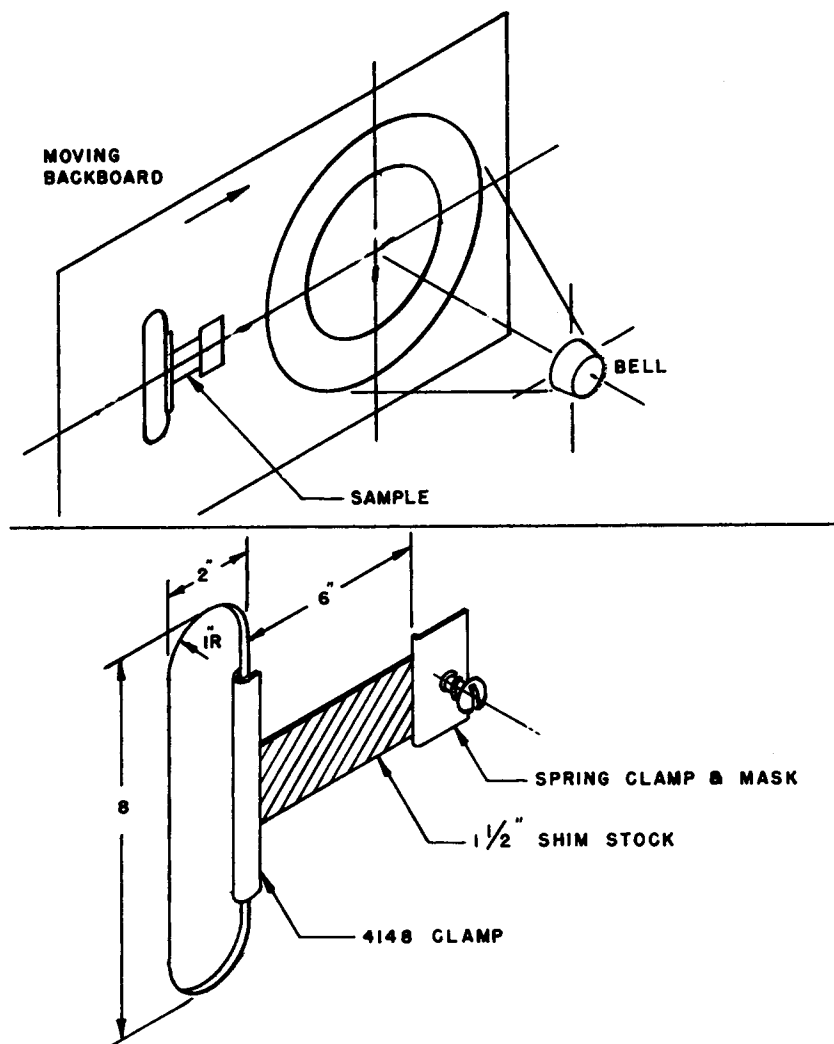
Fig. 2. Schematic of arrangement for determining wraparound (or collection) efficiency of particles which intercept porthole in target.

factors which might be expected to dictate to a more or less degree the behavior of that material.   It would be surprising if any single one of these was the determining factor governing the electrostatic behavior of all coating materials.

To evaluate the effect of different paint compositions and these various properties of each composition it is first necessary to establish some method or standard by which spray patterns can be compared.   The annular or doughnut-shaped pattern produced by a single bell on a flat surface is one that can be produced most readily and which is studied most easily because it is most reproducible.   Since the mechanism of the disk and bell atom-
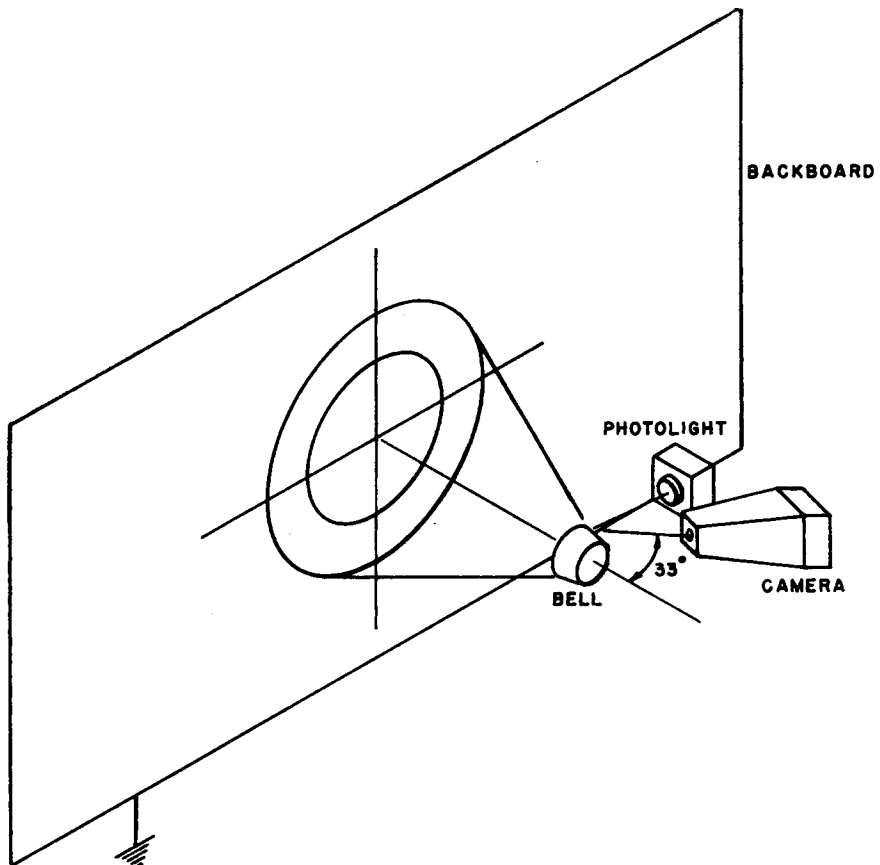
Fig. 3. Schematic of bell, target, and camera arrangement for photographing paint particles in flight.

izers are comparable, the results of any study on the bell can be extended directly to the disk.   To check the possibility of using the bell pattern as an indication of sprayability, a single bell was set up after the manner shown in Figure 2 and a wide variety of materials were sprayed with it at a standard applied potential of 100 kv.   The geometry of the patterns produced was studied in an effort to find some measurable features which would correlate directly and accurately with the overall response of a particular paint in electrostatic spraying.   No single feature of the spray pattern was found which by itself could be used as a quantitative parameter in providing a rating scale significant to trained observers.   Several features, however, were found to be of importance, and when considered together, these provided, when combined, the one quantitative measure here desired.

One aspect of the spray pattern which appears to offer the greatest possibility of determining suitability of paints in electrostatic spraying is the size of the atomized paint particles.   By photographing the region of the bell edge with a high speed camera (Fig. 3), it was possible to arrest the
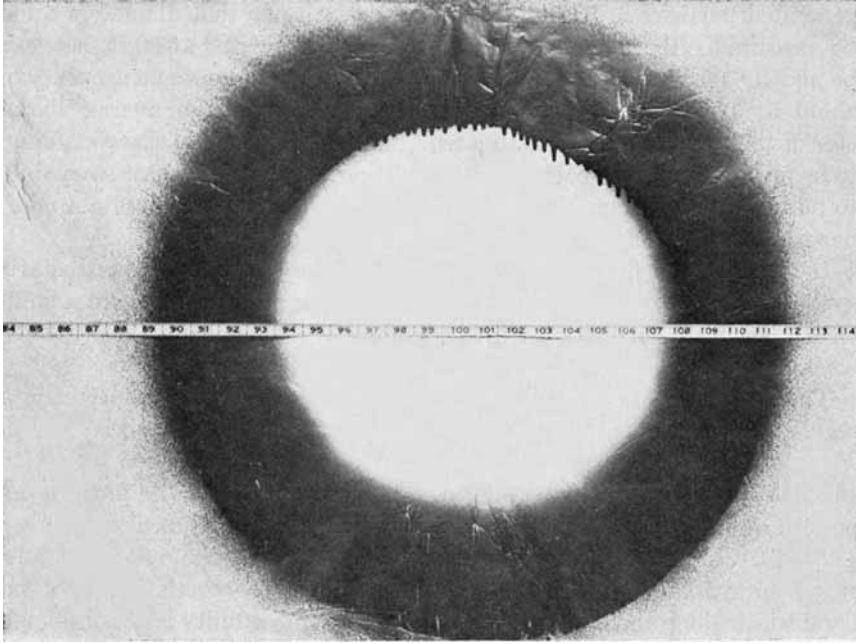
Fig. 4. Measurement of band width on aluminum foil target; poor dispersion; narrow fan at target distance of 12 in. from atomizing bell; delivery rate 100 cc./min., 100 kv., 900 rpm on bell.
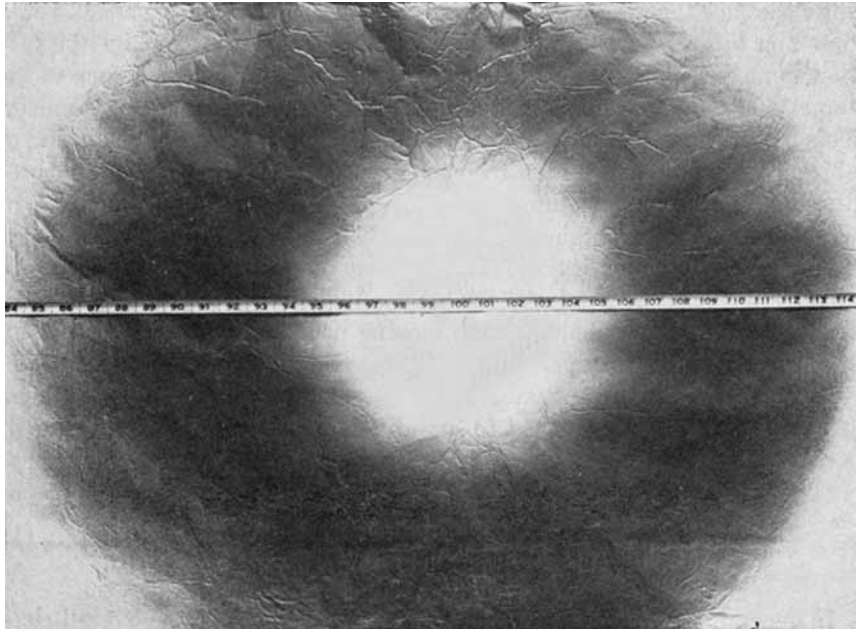

Fig. 5. Same conditions as in Fig. 4, but with paint upgraded to have improved band width.

generated particles in flight with sufficient clarity so that diameters could be measured. By using a 1 μsec. flash, particles moving at 50 ft./sec. can be photographed as clear spherical images (Fig. 1). Size, to an accuracy of about 10%, can be determined from enlarged prints, and an average diameter of the particles can be estimated. In general, particle size was found to be fairly uniform for each special condition; hence, it was necessary only to measure and average the diameter of 50–100 particles to obtain a number which reasonably reflected particle size.

In general, the finer the particles, the better the overall electrostatic sprayability. However, particle diameter alone does not provide a sufficiently accurate correlation with the subjective judgment of experienced observers who are concerned with the total overall result.

The particle cloud which is generated from the bell edge disperses in a regular pattern as it moves to the grounded target where a band is formed. The degree of this dispersion appears to offer a second index by which suitability of paint might be judged. The band width of the pattern deposited on a target at 12 in. distance from the bell can be measured (Figs. 4 and 5). In general, the wider the band, the better the overall electrostatic sprayability. Again, a sufficiently accurate correlation between band width alone and expert judgment on total sprayability is not obtained. Further, band width does not always correlate with the particle size criterion.

Another important attribute of electrostatic spraying is the ability of the field to deflect the spray particles and to deposit them upon the target despite the fact that the initial trajectory of the particle, if extended, would miss the target. This improved deposition is demonstrated by the fact that some of the particles which do miss the target are deflected back to the target and deposited on its surfaces not directly exposed to the atomizer. This factor, termed "wraparound," is of particular value in the painting of objects like chair legs and wire fencing. Difference in wraparound produced with different paints suggests a third criterion. A measure of wraparound may be obtained by moving past the spray head at controlled speed, two nearly identical target strips, one of which shows only one face directly to the spray head and the other of which is so positioned with respect to a standard opening in the moving backboard as to collect on its surface only those spray particles which pass through the opening and then wrap around. This arrangement is shown schematically in Figure 4. The strips are then suitably baked to dry the paint and wraparound ratio W is calculated according to eq. (1):

$$W = \frac{\text{Wt. of dry paint on back strip}}{\text{Wt. of dry paint on front strip}} \tag{1}$$

In general, the higher the wraparound ratio, the better the overall electrostatic sprayability, but correlation of wraparound ratio alone with expert judgment is not sufficient index for rating total quality of electrospraying.

Several hundred experiments have been conducted using different materials and a figure for particle diameter D, wraparound ratio W, and band width B for each of these has been determined. In addition the manner in which each of these materials behaved electrostatically was rated by a group of ten or more trained observers. It has been found that the expert evaluation and a dimensionless quantity termed "figure of merit" F derived from the above three factors gives excellent correlation. This quantity is defined by eq. (2):

$$F = WB \text{ (in inches)}/10D \text{ (in inches)} \tag{2}$$

The factor of $1/10$ is introduced only as a convenience to have F always greater than unity.

In this formula an increase in band width B or wraparound ratio W or a decrease in particle size D will all increase the figure of merit. The figure of merit (a dimensionless number) tends to range from about 1 for poor paints to about 60 or more for excellent paints. Experimentally, the accuracy of determination of F is about 10% at values where F exceeds 10; accuracy is less than 100% for values less than 5. In brief, an increase in F of about 10 or 15 indicates a significant improvement in electrostatic sprayability, judged subjectively by all of 10 or more observers experienced in the art. Hence, within these limits, numerical figures can be used as a reliable guide to classify paints as poor, fair, good, or excellent for electrostatic spray purposes. The figure of merit thus measures the ability of the paint to be efficiently electrostatically atomized, dispersed, and deposited as a film. When the figure of merit exceeds 70, further subjective distinctions by skilled observers are difficult to make. All paints above this figure are very good. Leveling and appearance of film deposited do not enter into the value of F. However, in general, at high values of F, leveling and appearance were good. This appearance factor conditions the reaction of observers of the above effect, but it does not appear as one of the quantitative factors in the ratio defining F.

By using the above defined figure of merit, coating materials can now be tested and compared in terms of their electrostatic applicability. It is possible now to investigate systematically how variation of the formulation, particularly the incorporation of specific additives, can upgrade paints in this respect.

It is also possible through use of the figure of merit to evaluate the correlation which exists between this measure of electrostatic sprayability and the other characteristics of coating materials such as d.c. electric conductivity, dielectric constant, a.c. conductivity, dissipation factor, surface tension, and viscosity.

It is a common but erroneous belief that no matter what kind of coating material is used, the addition of a properly selected thinner can adjust the paint for successful electrostatic application. For example, when solvents have a greater dipole character than the resin binder, it is generally believed that the spray performance is influenced more by the solvent than by the

resin binder.   Using the figure of merit as a basis of comparison, we have
investigated the soundness of this approach.   It is now evident that the
total constitution of the vehicle, including pigments, additives, binder, and
thinner, must be considered in defining the variables which control spray
behavior of coating materials.   Our research effort disclosed that nonve-
hicle components of the paint can also be very important, and sometimes
trace additives can be even more important than the major constituents
such as pigment, binder, and thinner.   The fact also emerged that under
some conditions the design of electrospray process equipment can be of far
less importance than proper chemical design of the material being applied.

For a considerable period of time it has been recognized[1] that a coating
material should have reasonable electrical conductivity if it was to be
sprayed successfully with electrostatic methods.   This motivated the
earlier and somewhat empirical practice of thinning paints with polar
solvents so as to adjust their conductivity into the correct range for electro-
static sprayability.   In general, solvents with the highest polarity were
found to have the greatest effect in reducing the electrical resistance of coat-
ing materials.   Those paints were widely used which readily had their con-
ductivity adjusted by the simple adjustment of solvent formulation.   This
relatively simple procedure has been very useful to paint formulators and
users of spray methods such as the Ransburg No. 2 bell and disk process.

Sometimes, however, the binder and solvent composition of a paint may
have such high resistivity to begin with that unreasonably large amounts
of high polar solvents are required to upgrade their conductivity.   Also,
it has been recognized that the addition of excessive quantities of strong
solvents in many cases impairs the quality of the paint film or the applica-
tion characteristics of these materials.   Such extreme dilution often results
in the sagging of the wet coat or the lifting of previous applied undercoats.
The addition of strong solvents in amounts sufficient to upgrade electro-
static sprayability has not always, therefore, been a practical remedy for a
large number of paints.   Such materials, up to now, have been considered
as having only limited applicability with electrostatic spraying.   It is this
group of paints with which we are concerned in this study.   We have at-
tempted to upgrade these materials by other methods.

A few illustrations will here be cited to demonstrate how major changes
can be produced in the figure of merit of a particular paint by making simple
formula modifications.

A basic formulation which does not handle well electrostatically and
therefore requires upgrading is provided by a long-oil, alkyd type paint,
pigmented with rutile TiO_2, when thinned with only mineral spirits to a
viscosity of 20 sec. (No. 4 Ford cup at 77°F.).   This is a typical example of
a paint type which behaves rather poorly when attempts are made to apply
it using electrostatic methods.   When evaluated it has a figure of merit of 9.

To illustrate how a paint with a low figure of merit and hence poor
sprayability can be upgraded a number of examples, which are long and
short alkyds, are described with their characteristics in Tables I–VI.

TABLE I
Use of Methyl Isobutyl Ketone in the Oil-Alkyd
Paint Thinned with Mineral Spirits

Conductivity (d.c., 100 kv.), μamp.	Methyl isobutyl ketone (based on paint), %	Amine-treated Bentonite (based on pigment), %	Figure of merit F
0.5	4	0	16
1.5	4	2.6	15
0.8	7.5	0	20
3.0	7.5	2.6	25
1.3	11.5	0	13
6.9	11.5	2.6	29
2.0	14.5	0	16
19.1	14.5	2.6	59

TABLE II
Modification of a Commercial Automotive Primer[a]

Polar solvent[b]	Bentonite added (based on pigment), %	H. V. conductivity, μamp.	Band width B, in.	Wrap-around ratio W	Avg. particle size D, in.	Figure of merit F
Isopropyl alcohol (7.2%)	0	3.5	3.7	0.0020	0.0026	3
Ethylene glycol monomethyl ether (7.2%)	0	5	4.5	0.0031	0.0021	7
Ethylene glycol monomethyl ether (9.7%)	1.2	36	9	0.0073	0.0017	39

[a] Vehicle is ester of oxidizing fatty acids and low molecular weight polymers derived from reaction of epichlorhydrin and bisphenol A, dissolved mainly in hydrocarbon solvent. Pigmentation is with red oxide and filler pigments at pigment volume concentration sufficiently high to produce flat and sandable finish.

[b] Viscosity reduced to 16 sec. (No. 4 Ford cup at 77°F.) by polar solvent addition.

Specifically Table I is for a simple paint composition made up by dispersing 24 vol.-% of rutile, titanium dioxide in a soya-modified, pentaerythritol-type alkyd (24% phthalic anhydride) in mineral spirits (Kauri butanol value of about 38; boiling point range 318–386°F.). This material is a 50% solids paint. The separate and combined effects of increasing amounts of solvent and of one particulate additive, amine-treated Bentonite (National Lead Co.),* on figure of merit, are shown. The conductivity of this paint was measured with an apparatus as illustrated in the diagram on Figure 6. A quantity of the material was inserted into an insulating

* This is a trade name for a product obtained when a clay material, montmorillonite, is subjected to certain exchange reaction, with alkyd amines.[7]
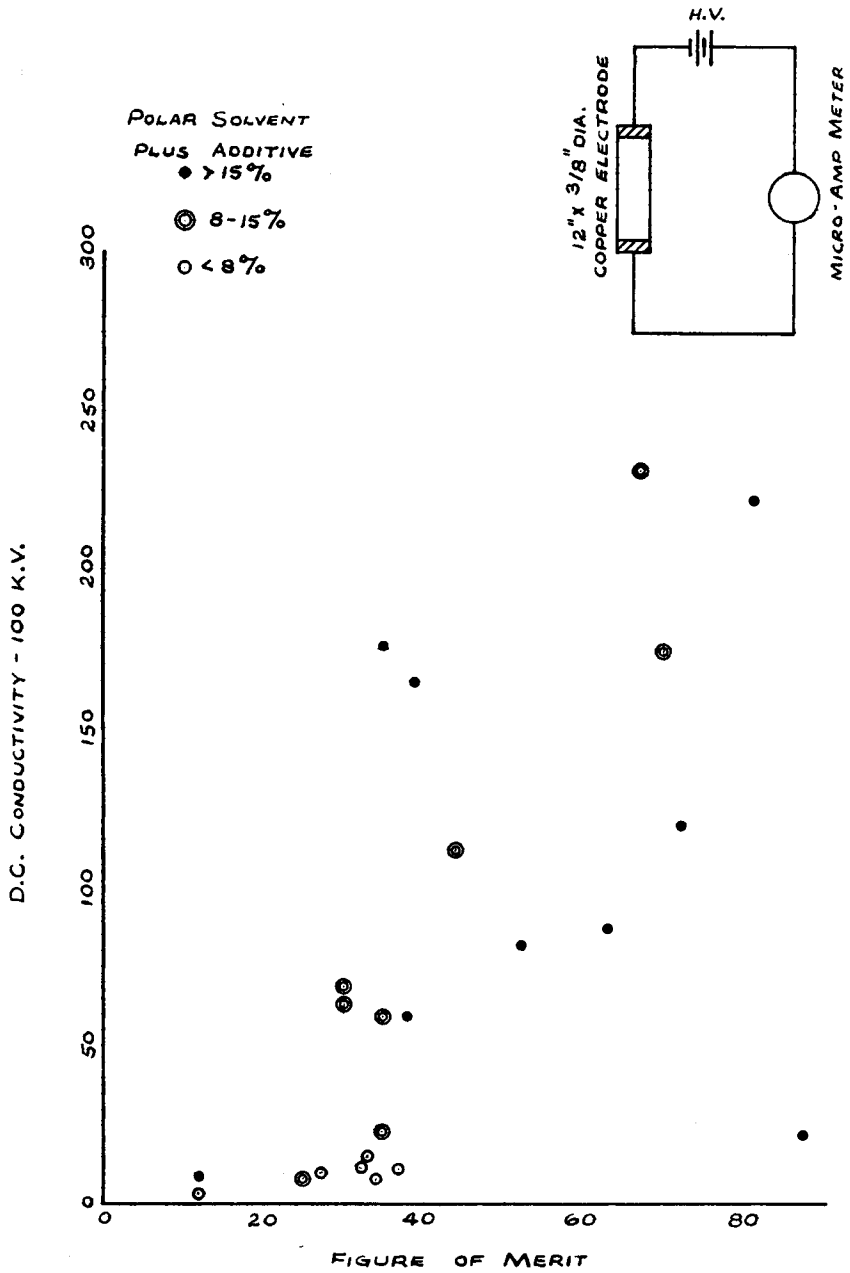
Fig. 6. The d.c. conductivity of paint (measured across copper electrodes of ³/₈ in. diameter in 12 × ³/₈ in. polyethylene tube filled with paint, at 100 kv.). Correlated with figure of merit for variety of paints.

TABLE III

Alkyd Paint (24 Vol.-% TiO₂) Thinned with Xylol and Different Types of Polar
Solvents at 20 sec. No. 4 Ford Cup Viscosity

Polar solvent	Hydrogen-bonding capacity	H. V. conductivity, μamp.	Band width B, in.	Figure of merit F
Xylol	Weak	0.5	6.00	9
Butyl Acetate (15.3%)	Moderate	0.75	6.00	15
MIBK (14.5%)	Moderate	2.0	5.50	16
2-Nitropropane (9.2%)	Weak	3.5	6.50	27
Nitromethane (12.8%)	Weak	15.0	8.30	43
Methyl cellosolve (12.5%)	Moderate	22.5	9.50	66
Methanol (6.3%)	Strong	23.5	8.5	50

TABLE IV

Effect of Amine Type Additives on Electrostatic Spray
Performance in an Alkyd Paint (24 Vol.-% TiO₂)

Additive	Solvent	H. V. conductivity, μamp.	Figure of merit F
—	Butyl acetate (4%)	0.75	8.5
Triethylamine (1.5%)	Butyl acetate (4%)	2.30	10.0
2-Nitro-1-butanol (2.0%)	Isopropyl alcohol (3%)	1.90	15.0
Armeen-DM 18D (1%)[a]	Nitromethane (4%)	5.75	19.0
Ethoduomeen T-13 (1.5%)[a]	Nitromethane (1%) + butyl acetate (3%)	22.50	33.7
Armeen-DM 18D (1%)[a]	Nitromethane (11%)	135.00	43.0
Armeen M2C (2%)[a]	Nitromethane (4%)	35.50	54.0

[a] Trade names, Armour Ind. Chem. Co.

tube ³/₈ in. in diameter and between two electrodes 12 in. apart. A d.c. high voltage of 100 kv. was impressed across the electrodes, and the current passing through the material was observed. It is noted that the conductivity of this material was too low to be measurable with this apparatus without addition of a minimum of 4% of ketone. Addition of higher amounts of the solvent increased the conductivity but had little effect on the figure of merit of this material. Addition of large volumes of the more polar solvent is impractical and results in sagging, intercoat lifting, and low film thickness.

The significant effect observed was the great efficiency of the amine-treated clay when added in the presence of the ketone in amounts of less than 3% by weight of pigment during grinding on the three-roll mil. This enhanced the conductivity and markedly upgraded the figure of merit.

In Table II, a commercial automotive primer was examined and 0.5 high voltage conductivity and its figure of merit evaluated as a function of Bentonite and polar solvent additions. Again the marked increase in the

figure of merit with simultaneous addition of both the polar solvent and the Bentonite is noted.

In Tables III and IV the effect of additives on the sprayability of an alkyd paint (24 vol.-% TiO_2) is summarized. In Table III the additives are various solvents having different hydrogen-bonding capacities. In Table IV the influence of amine type additives of varying molecular weights when combined with solvents having varying hydrogen bonding capacity is recorded.

Tables V and VI show the effect of similar additives on a linseed oil house paint and an oil-alkyd paint thinned with mineral spirits.

TABLE V

Modification of a Typical Commercial Type of Linseed Oil House Paint through Addition of Polar Solvent and Bentone #34 (Thinned to 20 sec. No. 4 Ford Cup at 25°F.)

Benton-ite, %	MEK, %	H. V. conduc-tivity, μamp.	Band width B, in.	Avg. particle size D, in.	Figure of merit F
0	0	2.3	4	0.0043	1
0	7.0	4.9	5	0.0030	6
1.2	0	2.1	5.5	0.0031	4
1.2	7.1	17.0	9.5	0.0021	32

TABLE VI

Use of 2-Nitropropane in the Oil-Alkyd Paint Thinned to 20 sec. with Mineral Spirits

2-Nitropropane (based on paint), %	Bentonite salt (based on pigment), %	Conductivity (d.c., 100 kv.), μamp.	Figure of merit F
3.7	0	0.75	17
3.1	0.5	1.2	22
6.0	0	1.0	25
5.2	0.5	3.9	38
9.2	0	3.5	27
7.8	0.5	10.5	44

Conductivity does not seem to be a completely definitive condition in regulating values of the figure of merit. If data of Tables I–VI are collected along with other data for other paints to reconstruct a correlation curve of conductivity verses figure of merit (Fig. 6), a general trend seems to exist. However, the data are widely scattered about any possible correlation curve. Where conductivity is varied by using less than a total of 15% in weight of solvent plus other additives, the breakdown of a clearly defined correlation between conductivity and figure of merit is most severe. In this most interesting class of minor modifications of a low conductivity
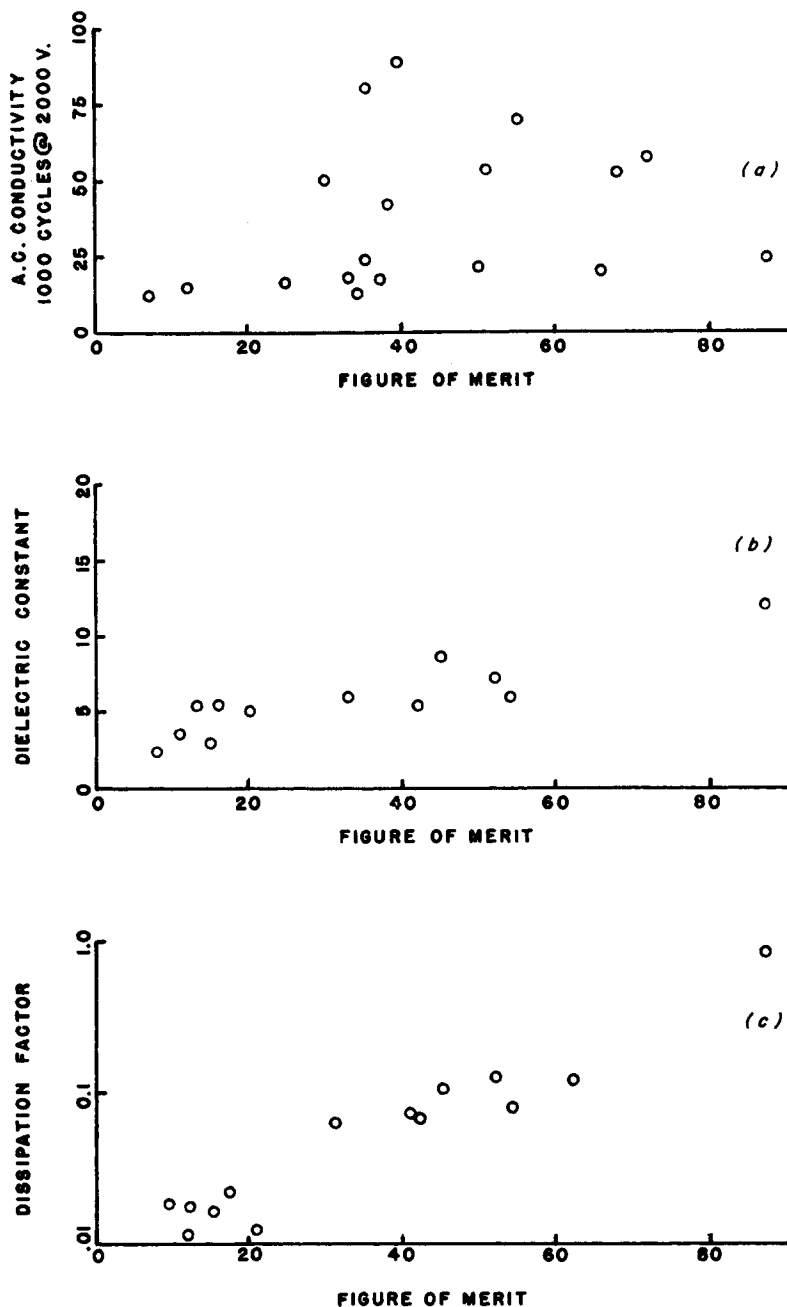
Fig. 7. Figure of merit correlations with (a) a.c. conductivity (measured at 1000 cycles/sec., 2000 v. between $^3/_4$ in. diameter copper electrodes, $1^3/_4$ in. apart, immersed in polyethylene container filled with paint; (b) dielectric constant at 10 kcycles of several paints; (c) dissipation factor at 10 kcycles.

paint, specific additives have specific and different degrees of effectiveness on both conductivity and other factors governing the parameters which define the figure of merit.

Figure 7 shows three graphs of similar attempts to correlate F with dielectric constant, alternating current conductivity at 1000 cycles/sec. and dissipation factor. The three graphs describe many measurements on a variety of paints including some not described in this paper. The general intent is to show the failure of definitive correlations of F with ordinary, and perhaps somewhat crude, measurements of electrical properties of the total paint at its spraying composition.

The same lack of correlation is obvious in Table VII, where attempts were made to relate F to surface tension.

TABLE VII

Effect of Surface Tension on Electrostatic Sprayability
of Paints (20 sec. No. 4 Ford Cup Viscosity)

Type of paint	Polar solvent	H. V. conductivity, μamp.	Surface tension, dyne/cm.	Figure of merit F
Linseed alkyd paint	—	1.5	29.3	2.6
Linseed alkyd paint	Butyl acetate (9.8%)	3.5	27.6	5.0
Linseed alkyd paint	Butyl acetate (9.8%) + nitromethane (3.7%)	2.0	28.1	13.8
Linseed alkyd paint	Acetone (13.8%)	21.0	27.3	27.1
Linseed alkyd paint[a]	Butyl acetate (6%) + nitromethane (18%)	237.0	29.5	54.8
Alkyd-amino paint	—	19.0	29.3	45.5
Alkyd-amino paint	Butyl acetate (7.5%) + nitromethane (7.5%)	485.0	29.0	57.4

[a] Additive: Bentone #34 (National Lead Co.).

The fact has often been observed that introduction of small amounts of additives can change markedly the rheology of paint. Early in this study it seemed feasible to relate electrospray characteristics to differences in rheology measured by techniques which did not involve superposition of high voltage fields to perturb the flow process. A study was conducted to examine the validity of this relationship. Six long-oil alkyd paints pigmented with rutile TiO_2 and thinned with mineral spirits and polar solvents to a viscosity of 20 sec. (No. 4 Ford cup at 77°F.) were used for this purpose. These materials are described in Table VIII. Figures 8 and 9 show data obtained on these materials with two different types of viscometers. The Squibb viscometer[3] for low shear viscometry, developed by Myers and Zettlemoyer, has been used to determine the values demonstrated in the Figure 8. These determinations were made at 27°C. The Figure 9 shows the values obtained with the capillary viscometer[4] at 30°C. The temperatures were different, different viscometers were used,

and sample ages were different.   Complete concordance of quantitative data cannot be expected; however, both measurements clearly separate the six alkyd paint samples (Table VIII) into those which show Newtonian and non-Newtonian behavior at low shear rates.
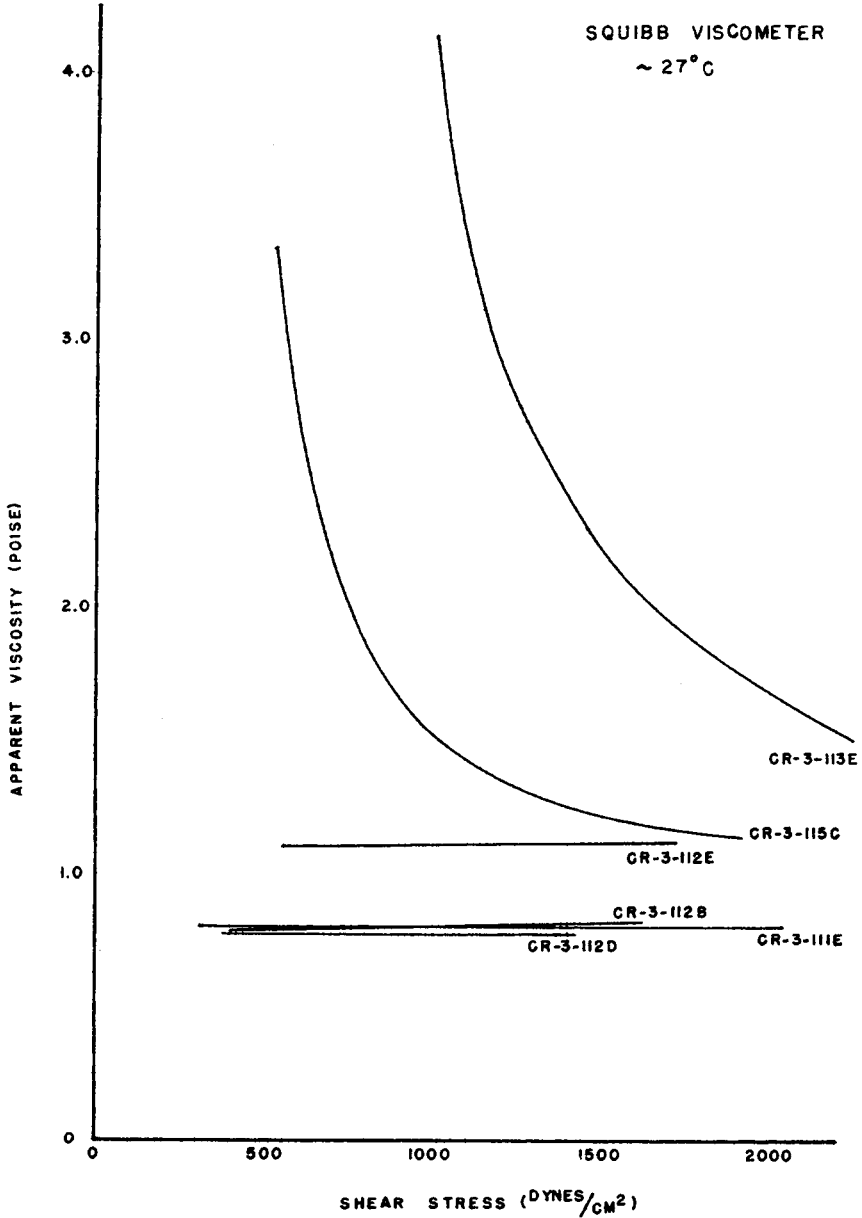

Fig. 8. Viscosity of paints of Table VII (variably upgraded oil-type house paints) measured with Squibb viscometer,

TABLE VIII

Electrostatic Spray Efficiency Related to Viscosities of White Alkyd Paint (20 sec. No. 4 Ford Cup, 77°F.)

| Code: CR-3	Conductivity, μamp.		Polar solvent	Additive	Shear stress, dyne/cm.²	Viscosity, poise	Figure of merit F
	d.c. 100 kv.	a.c. 2000 v.					
111-E[a]	7.5	16.5	Nitromethane (8%)	—	34–1390	0.366	43
112-E[a]	14.6	13.0	Nitromethane (16%)	—	18–870	0.293	38
112-B[a]	4.9	13.0	Methyl cellosolve (8%)	—	32–1400	0.325	31
112-D[a]	86.0	57.0	Methyl cellosolve (18%)	—	31–1390	0.385	63
113-E	92.0	58.0	Nitromethane (8%)	Bentone #34 (2.6%)	45–1400	1.250–0.547	73
115-C	16.0	17.5	Methyl cellosolve (8%)	Bentone #34 (2.6%)	40–1395	1.057–0.572	62

[a] Newtonian.
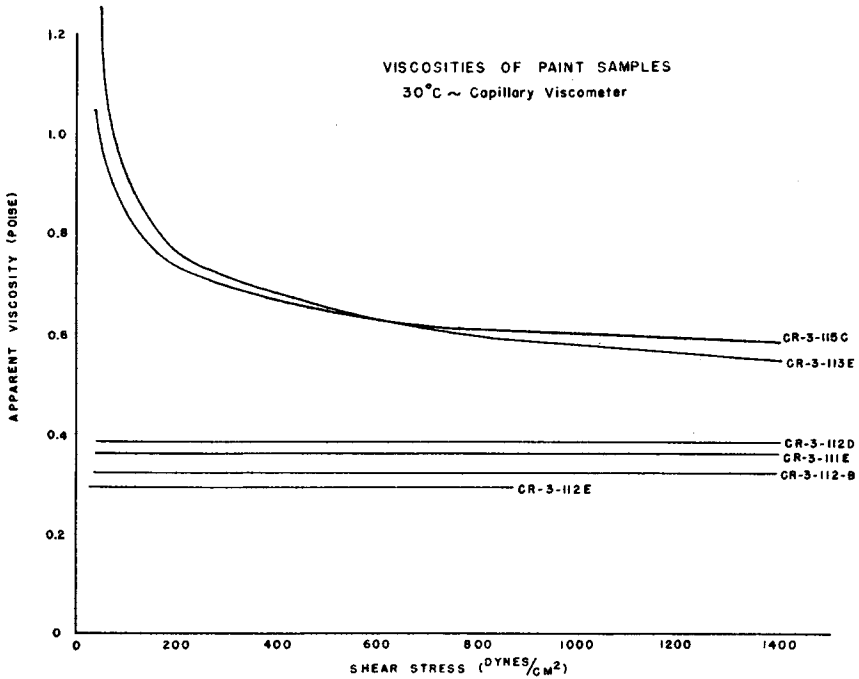
Fig. 9. Viscosity of same paints as in Fig. 8, measured with capillary viscometer.

Table VIII also shows the figure of merit and other data for the six alkyd paints for which viscosity data are described in Figures 8 and 9. Two of the paints showing non-Newtonian flow curves at low shear rate have a high figure of merit for electrospray efficiency. One other having a high figure of merit shows Newtonian behavior. Throughout this study exceptions of this sort occurred with sufficient frequency to cast doubt on validity of attempts to correlate electrostatic spray efficiency with easily measurable distinctions in flow behavior in the absence of electrical fields. There is little doubt that viscosity is important, but definitive values of this factor cannot be determined easily using convenient experiments.

Viscosity discriminations of the precision shown in Figures 8 and 9 are not easy to make. The differences in viscosity are relatively small between specimens which differ much in electrospray characteristics. Viscosity measurements made with the Ford cup or other industrial control instruments would miss the distinction because of lack of sensitivity or precision, or because they are inappropriate for the flow rates characteristic of this process equipment.

Before much can be made of viscosity correlations, much work would be necessary, including determinations of how high voltage electrical fields affect fluid flow in heterogeneous systems at different shear rates.

These types of observations indicate that the hydrogen-bonding capacity of solvent or additive alone cannot be responsible for the upgrading of

electrostatic spray performance.   We suggest that certain unique combinations of additives may be especially important.   To achieve the best result, the paint should contain: (a) particulate component, having proton donor groups on the surface capable of hydrogen bonding with a base; (b) strong base which can accept hydrogen bonding, and thereby become associated with the particles defined as the first component; (c) polar material of high dielectric constant, which is compatible with the continuum of the paint, and is not a strong enough base itself to compete with the groups on the particle surface in hydrogen-bonding reactivity with component b.   This third material may solvate and promote ionization of the complex formed by reaction of a and b.

Data of Tables V and VI suggest that if a paint lacks any of these functional components, the most desirable condition does not develop to a sufficient degree, and the paint will exhibit inferior electrostatic sprayability.   In some paint formulations, the minimum requirements are satisfied because materials included for other reasons have capacity to promote development of a fluid structure which can be atomized easily by electrical fields.   In a large number of instances, chance will dictate that one or more of the important elements of the composition are absent or, if present, may lack best efficiency in developing highly charged particles.   In these instances, defects can be overcome by additives.   The preferred art would recommend that adjustment of defective paints should be accomplished with minimal quantities of additives so as to minimize the hazards of creating other problems of control of the painting process of damage to paint quality. The three-component coaction hypothesis seems to serve as a tentative guide to experiments directed toward accomplishing the desired effect with minimal modification of composition of paints which have other desirable properties.   It puts emphasis on the possibility that the fault of limited conductivity in the continuum of the vehicle can be overcome by presence of a relatively low concentration of highly charged colloidal particles.

This hypothesis assigns an important role to the presence of highly charged colloidal particles in promoting improved spray efficiency in a favorably mixed solvent.   The efficiency of amine exchanged in clays as an additive has already been noted.

The data of Tables IX and X represent an attempt to test the plausibility of the hypothesis by incorporating additives which might react with particles already in the paint and increase their efficiency by increasing their ionic charge.   The only clearly defined particulate phase present in the sample paint used here was titanium dioxide.   This would need to adsorb charged surfactant molecules to increase surface charge density.   However, recent data[5] on alkyds seems to indicate that alkyd vehicles of this type can contain a dispersed colloidal gel in particle form when reacted to sufficient completeness to have good air-drying properties.   Such a colloidal phase might collect hydrogen-bonding components by ion exchange in the carboxyl group, or by adsorption, or it might react with metal ions so as to make phase separation more complete.

TABLE IX

Electrostatic Spray Performance Related to Dielectric Constant of White Alkyd Paint
(20 sec. No. 4 Ford Cup Viscosity at Feed to Spray Gun)

Conductivity, μamp.		Polar solvent	Additive	Dielectric constant (10 kcycles)	Figure of merit F
d.c., 100 kv.	a.c., 2000 v.				
2.25	12.5	—	—	3.04	9.0
1.75	12.5	Nitromethane (4%)	—	4.67	20.0
12.70	17.8	Nitromethane (6%)	—	8.90	19.0
0.75	11.0	Butyl acetate (4%)	—	2.75	8.5
235.0	600.0	Nitromethane (3.5%) + butyl acetate (8.0%)	Bentone #34 (1%)	7.52	51.8
35.5	27.0	Nitromethane (3.5%) + butyl acetate (8.0%)	Armeen M2 C (2%)	6	54.0
35.0	28.0	Methyl cellosolve (12%)	—	5.18	42.0
50.0	37.0	Nitromethane (7%)	Triethylamine	5.58	41.9

TABLE X

Use of Additive in the Alkyd Paint
(24 Vol.-% TiO_2, 50% Total Solids)
Thinned with Different Solvents (20 sec. No. 4 Ford Cup)

Conductivity (d.c., 100 kv.) μamp.	Solvent	Additive	Figure of merit F
0.5	Xylol	—	2.6
2.1	Butyl acetate (9%) + nitromethane (3%)	—	12.0
4.0	Butyl acetate (4%) + nitromethane (4%)	Zn (0.92%)[a]	12.0
5.5	Butyl acetate (7%) + nitromethane (7%)	Zn (0.25%)[a]	24.0
3.3	Butyl acetate (9%) + nitromethane (3%)	Zn (0.13%)[a]	26.0

[a] Zinc naphthanate soap (added as 6% solution in solvent which is mainly mineral spirits).

Table X shows some effects of adding zinc soap and several amines which may adsorb on titanium or could react with carboxyl groups on alkyd in macromolecules (or micelles) to form highly charged and insoluble particles.

Also, heavy metal soaps may not be true solutions, but may also have a micellar structure in organic media similar to that shown by aqueous soaps above their critical micelle concentration.

Obviously, if attempts are made to fit the data to the general hypothesis, a variety of plausible ways can be imagined for producing in the low conductivity fluid continuum of the vehicle some sort of charged particle.

Some of these particles may have a size and charge density, and local dielectric environment so they are more effective than others. Much research still needs to be done before we can develop a firm theory of electrical microstructure of fluids. For the present, the hypothesis we propose has only tentative value in guiding practical attempts to solve problems of upgrading the electrospraying process.

The effects of adding the supposedly missing component to promote *in situ* development of charged particles are shown in Tables IX and X. Possibly the effects are not explained by the hypothesis which motivate the test. It is confirmed again, however, that the figure of merit does not follow conductivity as a regular correlation, and different combinations of additives have highly specific effects upon both conductivity and sprayability. Even in a practical sense, use of this hypothesis requires some guides in distinguishing among additives of high dielectric constant and dipole movement, depending on whether they are strong or relatively weak in hydrogen-bonding capacity. One useful way is suggested by the infrared techniques of Gordy and co-workers.[6] Many other techniques of assaying relative strength of acids and bases and ion-exchange or adsorption capacity of solids are common in the chemical literature. Emphasis on acid–base reactions with surfaces of colloidal particles comes from the greater certainty of predicting their possibility. Development of charge by physical adsorption of ions may also occur, but the conditions determining this are more difficult to understand and to regulate in efforts to modify a paint.

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Résumé

On décrit quelques méthodes pour déterminer la dimension de gouttelettes D de peinture atomisée dans un champ électrostatique. On donne également une méthode pour estimer la largeur de bande B et le coefficient de recouvrement W d'un film produit dans des conditions standardisées. Une façon de définer de manière quantitative la qualité de la peinture F est d'utiliser comme mesure le rapport BW/D qui peut être relié à des aberrations qualitatives de l'efficacité de pulvérisation. Cette mesure quantitative fournit un guide plus efficace lors d'expériences destinées à améliorer l'exécution de la pulvérisation électrostatique d'autres peintures intéressantes. On montre par quelques exemples que l'incorporation de particules colloïdales fortement chargées augmente de manière significative l'efficacité de la pulvérisation électrostatique des peintures que contiennent des particules de faible conductivité.

Zusammenfassung

Methoden zur Bestimmung der Teilchengröss D eines in einem elektrostatischen Feld zersprühten Anstrichstoffes und zur Messung der Bandbreite B und des Umhüllungsverhältnisses W eines unter Standardbedingungen erzeugten Films werden beschrieben. Eine quantitative "Figure of Merit" F, definiert als das Verhältnis BW/D kann zu den qualitativen Abweichungen der Elektrospraywirksamkeit in Beziehung gesetzt werden. Dieses quantitative Mass bildet eine recht wirksame Richtlinie für die Ausführung von Versuchen zur Verbesserung des Elektrosprayverhaltens von sonst brauchbaren Anstrichstoffen. Einige Beispiele werden angegeben, die zeigen, dass der Einbau hochgeladener kolloider Teilchen einen merklichen Einfluss auf die Elektrospraywirksamkeit von Anstrichstoffen mit Trägern niedriger Leitfähigkeit besitzt.