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Cross Reference: Punch Card Index

MARSHALL LABORATORY
August 15, 1951

MEMORANDUM REPORT NO. M-378

GORDON RESEARCH CONFERENCES

A.A.A.S. 1951 - SECTION ON ORGANIC COATINGS

JUNE 18 - 22, 1951

SUMMARY:

The largest, and most interesting, portion of the program was devoted to films from undissolved polymers. These included organosols, plastisols, latices, cellulose and fibrin. All large companies in the finishes field appear to have research in progress in this broad subject judging from the questions asked by the audience.

Other items of particular interest are the preparation of methacrylate modified alkyds, the statistical study of pinholing which involved new techniques, the use of mechanical property measurements to measure film deterioration (all at Rohm & Haas), the study of fibrin films which are really fibrous mats (at University of Wisconsin), the study of the relationship between thickeners and emulsifiers in latices (Dow), the study of the electrical properties of films (Westinghouse), and viscosity studies on plastisols (Goodrich).

The fundamental study of electrical properties of film forming materials is something that we have neglected. It might give us a deeper insight into the structure of polymeric materials and might serve to improve our understanding of mechanical properties.

Participation in this conference was very instructive. It is recommended that it be continued on an annual basis. Also, it is likely that some of the speakers (particularly those sent by raw materials suppliers) might be asked to repeat their talks before our laboratory staff.

Sixty-four chemists from different paint companies and from suppliers attended the conference. O. H. Bullitt, Jr., Dale Herndon and S. Hochberg represented F. & F. The chairman was R. H. Kienle, of Calco Chemical Division, American Cyanamid Company. The papers presented are summarized below:

TABLE I

SOME DISPERSION RESINS

CODE	VCl%	SPEC. VISC.[1]	INTR. VISC.	PARTICLE DIAM.[2] MICRONS		
A	99+	.25		.2	.3	.7
VYNV	96	.29	1.60	.05	.12	.6
DX	91	.26		.05	.10	.6
C	95	.20		.08	.15	.6
NV3	99+	.30		.10	.75	.80
B	97	.24		.10	.80	1.30

1. Obtained by measuring viscosity of 0.2 gm. polymer in 100 cc. nitrobenzene.

2. Underlined figure shows number average. Fine and coarse range also indicated.

TABLE II

PARTICLE SIZE DISTRIBUTION IN A CLEAR VYNV ORGANOSOL

MICRONS	WT.% 48 HOURS BALL MILL GRINDING
0.0 - 0.5	54.5
0.5 - 1.0	31.5
1.0 - 2.0	12.0
2.0 - 3.0	2.0
3.0 -	0.0

PAPERS PRESENTED:

"Coatings from Organosol and Plastisol Dispersions"
by G. M. Powell of Carbide & Carbon Chemical Company

A large portion of the material discussed by Powell in this paper has been discussed in a paper by G. M. Powell, R. W. Quarles, C. I. Spessard, W. H. McKnight, and T. E. Mullen, entitled "Formulations Studies of Vinyl Resin Organosols", Mod. Plast. 28, p. 129 (June, 1951). Powell started his talk with a discussion of the particle size of various resins which may be made up into organosols or plastisols. Table I gives the data that he discussed. This table shows that there is a rather wide spread between the small size and the large size particle of the same resin. The VYNV type of resin is used in organosols mostly because of the small particle size, while the NV-3 type is used in plastisols. In general, large particle size is favored for plastisols because larger ratios of solid polymer to fluid dispersant are required in the finished product. Material of large particle size generally results in lower viscosity than the same weight of the material of small particle size.

Table II shows that the original particles of the solid organosol resin are not completely broken up in grinding an organosol in a ball mill. It also shows why great difficulty has been encountered in getting good gloss from a vinyl chloride organosol. Note that in this table there is a fair amount of material, fully 14%, above 1 micron in particle diameter. It is not expected that a material of this particle size could possibly result in a glossy organosol film.

Plastisols are generally made by thoroughly mixing the polymer powder with a plasticizer. After application to the proper substrate, the mixture is heated, and coalescence occurs. The tensile strength of the resulting product depends to a large degree on the plasticizer used. For example, if 60 parts of VYNV organosol are used to 24 parts of tricresyl phosphate, the tensile strength will be approximately 5,500 lbs./sq. in., but if the plasticizer is dioctyl phthalate, the tensile strength will be about 4,500 lbs./sq. in. If it is R2H, a polymeric plasticizer, the tensile strength will be on the order of 4,000 lbs./sq. in.

The viscosity of plastisols was studied by means of Brookfield and Interchemical Viscosimeters. It was found that as the resin content is increased, the viscosity remains very low up to some critical point, and at that point the viscosity rises very sharply. This would be typical of a well dispersed particulate system. In the case of the NV3 type resin, which is similar to the VYNV type, but of larger particle size, that critical concentration occurs at about 55% resin by volume. In general, the viscosity of the plastisol is determined to a great extent by the viscosity of the plasticizer.

Attempts were made to determine the mechanism for the decrease in viscosity or for the viscosity minimum that occurs when mixtures of solvents are used to disperse organosols. Electrophoresis experiments were performed which gave migration rates of 1.5 to 7 x 10^{-5} cm. sec./volt cm., that is about 1/10th to 1/100th of the migration rates in

aqueous systems. The mobility is a minimum in the neighborhood of the viscosity minimum. Original ionic impurities in the material do not seem to affect the results at all.

Vinyl chloride organosols seem to be difficult to adhere to most materials. However, several methods were proposed.

1. (a) To use an undercoat of wash primer, which consists largely of polyvinyl butyral.

(b) To use a topcoat which contains a polymer of the VAGH type (vinyl chloride, vinyl acetate, vinyl alcohol) which is dissolved in the solvent of the organosol.

2. It was suggested that a solution primer be used as a base coat and that the solution primer be selected for its good adhesion.

To increase adhesion to paper it was suggested that cationic wetting agents be used on the paper or in the organosol, as these cationic agents increase the penetration of organic materials into paper.

"Some Rheological Aspects of Vinyl Plastisols"
by W. D. Todd, B. F. Goodrich Chemical Company

Todd used an Interchemical Viscosimeter to measure the flow properties of plastisols. He found that plastisols show dilatancy, thixotrapy and yield point at the same time.

The plastisols are generally made from polyvinyl chloride compositions of large particle size, e.g., Geon 121, which has a rather uniform particle diameter of 2 microns. Geon 100X26S has much smaller particle size and a lower molecular weight. Geon 202 is a copolymer of vinylidine chloride and vinyl chloride of large particle size. Mixtures of polymers of different particle size may be used to obtain particular flow characteristics. For example, a mixture of Geon 121 - 22 parts, Geon 100X26S - 33 parts, Geon 202 - 45 parts and plasticizer - 65 parts has the same viscosity at several sheer rates.

The choice of plasticizer depends to some degree upon the aging characteristics desired. Dioctyl azelate and dioctyl sebacate age well and have a low viscosity. Tricresyl phosphate ages poorly.

When using pigments or fillers with plastisols an increased amount of plasticizer is used. The oil absorption of the pigment or filler should be measured, using the plasticizer that will be used in the organosol. The oil absorption figure obtained should be used to determine the extra amount of plasticizer to be added.

To obtain increases in viscosity several agents may be used in small quantity. The most interesting are (1) ethyl cellulose - 11 centipoise 483N-10, (2) bentone - No. 34 of National Lead, (3) Ceramid - of Glyco Products, (4) calcium stearate - made by Whitco.

TABLE III

CODE	VISC. $_{180}$	VISC. $_{20}$	YIELD PT. (dynes/cm.^{2})	D′	OBSERVED SPREADABILITY
1	13,000 cp.	3,400 cp.	0	2.17	Poor
8	52,000	11,000	0	0.72	Fair
13	13,000	8,500	3,000	0.41	Very good
18	12,000	2,700	0	2.86	Poor

The plasticizer used may be selected to give low viscosity. A typical formula of a low viscosity material would be Geon 121 - 100 parts; dioctyl sebacate - 15 parts; Flexol 4G0 - 15 parts; dioctyl phthalate - 32 parts; clay - 20 parts.

The rheological characteristics for plastisols of different types was then discussed:

For mold casting plastisols, viscosity should be low; yield value - none; dilatancy - small to moderate amount permissible. For slush molding plastisols viscosity should be low to medium, that is below 12,000 centipoise; there should be a low yield value with some thixotropy, a small amount of dilatancy not harmful. For spray application viscosity should be low, less than 2,000 centipoises; yield value - considerable amount desired; dilatancy - not desirable. An example was given having a spraying consistency at 66% solids.

Plastisols are often used in dip coatings. The object to be coated is heated and immersed in the plastisol. The Plastisol forms a gelled coating on the hot mold and then the mold is withdrawn. The viscosity desired is low to medium, about 12,000 centipoises; low yield values are generally desired and a small to a medium amount of dilatancy is permitted.

For special dip coatings on which there is to be no drip, agitated baths are used and the objects are removed very slowly and at an even rate. Low viscosity is desired - less than 2,000 centipoises; no dilatancy is permitted; and an appreciable yield value is necessary, "no less than 1/10th of the value of viscosity".

For glove coatings medium viscosity, below 12,000 centipoises; an appreciable yield value; and a low value of dilatancy is desired.

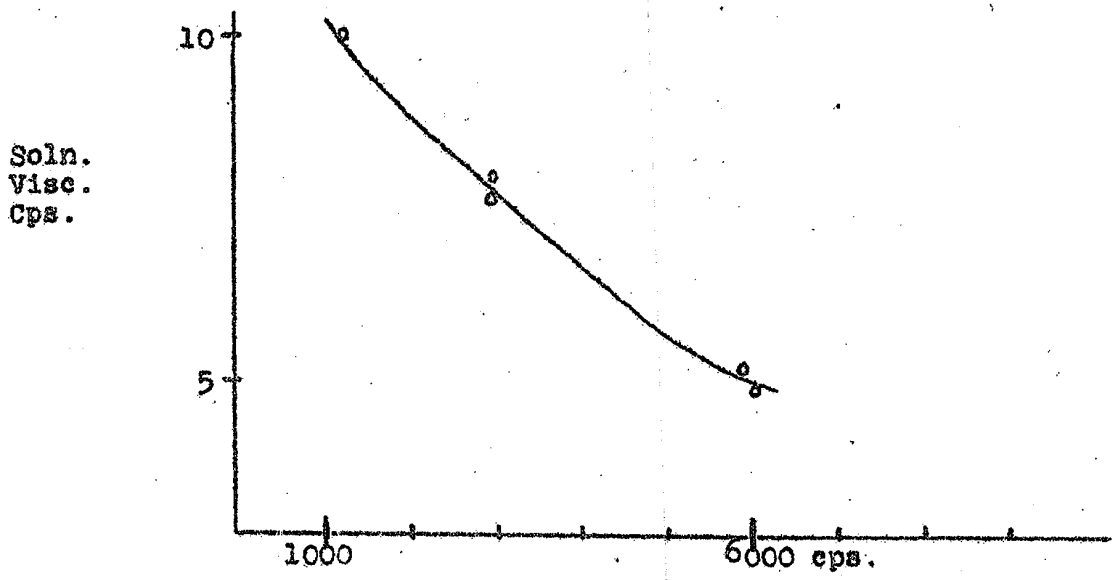
For spread coatings the characteristics will depend upon whether a deep penetration is desired into porous materials, or a shallow penetration is desired. For deep penetration a low viscosity, less than 2,000 centipoises; no yield value; and a low to medium dilatancy. For shallow panetration medium to high viscosity is desired, with an appreciable yield point and no dilatancy. For non-porous articles viscosity should be low to medium, yield point should be low to facilitate flowout, and dilatancy preferably low.

For plastisols to be used for spreading, a new hypothesis was developed to give a value for a term called "spreadability" which would correlate performance with viscosity measurements. The idea is to obtain coatings that could be put on rapidly in a knife coating type of machine without the phenomenon of "spitting". "Spitting" occurs when the coating does not go on smoothly but is pulled away from the fabric in very small areas. To measure spreadability, the viscosity at 180 rpm. and the viscosity of 20 rpm. are measured in the Interchemical instrument:

$$R = \text{Viscosity at 180 divided by viscosity at 20 rpm}$$
$$D = R \text{ minus } 1$$
$$D' = \frac{10{,}000 \times D}{\text{Viscosity at 180 rpm.}}$$

FIGURE 1

Effect of 1% of various emulsifiers on the viscosity of 0.25% methocel solution vs. its effect on a thickened latex containing 0.25% methocel.



and that is the measure of spreadability. The lowest value of D' is the best spreading. Table III shows examples of four plastisol materials, values for the viscosities and values for D', together with a rating for coatability or spreadability.

"Coatings - Properties of Synthetic Latices"
by O. R. McIntire (Saran Laboratory, Dow Chemical Company)

A big problem in the manufacture of polymer emulsions is the choice of emulsifier. This choice will depend to some degree on whether there is a step of coagulation later in the manufacturing process or whether the latex will be used directly. Choice of emulsifier influences its stability, its tendency to foam, the color of the finished product, its opacity. A wetting agent may or may not be permitted in the finished product, depending upon its use. Generally an emulsifier is used that would keep the viscosity low, but water sensitivity must be kept in mind. Degradation of the polymer in later use must also be kept in mind when picking an emulsifier. It is therefore almost standard practice to use several emulsifiers - first, small amounts during the polymerization step, and then additional amounts and perhaps different emulsifiers for increasing the stability of the finished product. The stability of the finished latex is influenced by the type of emulsifier used as stabilizer and by the particle size. Creaming generally results in the case of large particle size emulsions. This creaming does not necessarily result in breaking of the emulsion but merely a separation. The cream can be stirred in. Coagulation during storage is a common form of failure. Accelerated tests for storage stability are centrifuging and use of an oven. Stability to mechanical forces is generally tested with a Hamilton Beach mixer. Small particle size favors mechanical instability. Tolerance for foreign materials is another form of stability which is tested for. The methods for selection of emulsifier have not been worked out.

The addition of plasticizer to a latex in order to achieve softer and more desirable films (in some cases) may be done in several ways:

(1) Emulsions of a plasticizer are added to emulsions of the latex.

(2) Plasticizer may be added to the latex and subjected to mixing action.

(3) Casein or methocel may be added to the plasticizer. The latex may be added then in small amounts to the plasticizer with constant mixing. Larger and larger amounts are added until inversion occurs.

The time required for plasticizer-polymer equilibrium is sometimes fairly long. It is tested by centrifuging the mixture. If sufficient time has not been allowed then centrifuging will result in separation of the plasticizer. The time required may vary from

one hour to two or three days. In any case, better results with the finished film are obtained after the plasticizer-polymer mixture has been standing for some time. Heat, or a small amount of good solvent added to the plasticizer will speed this up.

The action of thickeners was discussed fairly thoroughly. Very small amounts of thickeners are effective. They are much more effective in latex than they are in water. Furthermore, the thickeners are more effective on small particle size emulsions than on larger ones. When the thickener has a large effect on the viscosity of the emulsion then, in general, good stability will result. Several explanations have been given for the increased effect of thickeners in latices over their effect in pure water:

(1) Water concentrates around the latex particles leaving the concentration of thickener higher in the free water phase. This explanation is not sufficient because too great a thickness of absorbed water would be required around the particles.

(2) There is interaction between the thickener and the emulsifier. Emulsifiers increase the thickening effect and the explanation is that bridges are formed between the particles as a result of the thickener reacting with the emulsifier. This explains the effect of small particles in increasing the thickening action and it explains the plastic flow of thickened dispersions. Data was shown on the effect of 1% of various emulsifiers on the viscosity of a methyl cellulose solution and this was compared with the effect of the same emulsifiers on a thickened latex - that is thickened with methyl cellulose. There was good correlation between them. Figure 1 shows the type of graph obtained.

Bridges obtained with the thickener are not easily broken by dilution. The viscosity that results from the addition of thickener is different, depending upon the method of addition. Data was given on the effect of different wetting agents, using a methocel thickener. It was shown that, if the wetting agent is Aresklene 375 very large effects are obtained as compared with Duponol ME, Aerosol OT, sodium stearate. The use of hydrophylic pigments decreases the viscosity of a methocel thickened dispersion. Other interesting items pointed out by McIntire included the use of styrene-maleic anhydride copolymer in an auxiliary emulsifier which generally improves the freeze-thaw stability; and the observation that addition of defoamers sometimes spoils freeze-thaw stability; pigments having soluble salts hurt the stability of the resulting mixture; glycol may be added to latices to improve the mobility towards the end of the drying process, and to get films which dry on heating.

"Coatings from Styrene-Butadiene-Drying Oil Emulsions"
by W. Bosch, North Dakota Agricultural College, Fargo, N. Dakota

Butadiene-styrene latex was mixed into a drying oil in the form of a water-in-oil emulsion. The mixture was dried and experiments were performed to determine whether any water was withheld in

the final product. No water was found, contrary to a paper that appeared in the literature some time ago.

"Properties of Films and Coatings of Biological Origin"
by J. D. Ferry, University of Wisconsin, Dept. of Chemistry

Cellulose fibers which may be laid down into a blotter like film are produced by bacterium xylenum. These fibers are approximately 300 angstroms wide.

Fibrinogen consists of fibers of approximately 35 angstroms by 700 angstroms with a molecular weight of 500,000. It forms clots at a concentration of 0.004% and a volume fraction of 0.00003. If a 15 millimeter clot is compressed gently to 3/10ths of a millimeter, a rubbery film is obtained which contains 70% water. The water can be replaced by a hydrophylic non-volatile plasticizer, for instance, glycerin. The films look and feel like highly plasticized vinyl resin. The finest strands have a diameter of 100 angstroms, which is 3 fibrinogen units in thickness and the length of hundreds of fibrinogen units end to end. The film may be swollen in one mol of acetic acid containing .05 mol of sodium chloride. The volume increases 2.4 times. The permeability of the fibrin films was measured. It is 0.2 cc. per hour per sq. centimeter per atmosphere pressure with liquid water on one side of the membrane being forced through. A calculation was made assuming that the pores are cylindrical. The openings are calculated to be on the order of 500-100 angstroms wide. Therefore hemoglobin with a 60 angstrom particle size filters through such a membrane but larger protein molecules do not. Armour supplies fibrinogen powder which contains approximately 60% fibrinogen at 40¢ per gm. At water contents of approximately 60% leathery films are obtained. The maximum tensile strength of a plasticized film is obtained at about 58% fibrinogen in the film and the maximum tensile strength is about 625 lbs./sq. in. with an elongation of 100%.

"Strength of Surface Coatings"
by R. Grinsfelder, Rohm & Haas Company, Philadelphia, Pa.

A quantity called toughness, which is the area under a stress strain curve obtained on a Scott Tester was used as a criterion for high strength. Measurements were made on a series of alkyd films, and tensile strengths, elongation and toughness values were given. The effect of accelerated weathering on the mechanical properties of a series of eight films was measured after exposure to high temperatures, to UV, and in the Weatherometer. (See Table IV). Methacrylate and acrylate modified alkyds were made. The effect on the toughness of various proportions of oil, acrylate, and glyceryl phthalate was measured. It is suspected that the acrylate used in these studies by Rohm & Haas is put in by way of the double bond rather than by way of ester interchange. Maximum toughness was obtained at a content of 30% acrylate, 40% glyceryl phthalate, 30% oil. On exposure in the Weatherometer, films containing about 25% glyceryl phthalate were best. These also contained 20-40% of oil.

FIGURE 2

PERCENT OF SAMPLES HAVING BREAKDOWN VOLTAGE LESS THAN INDICATED VOLTAGE

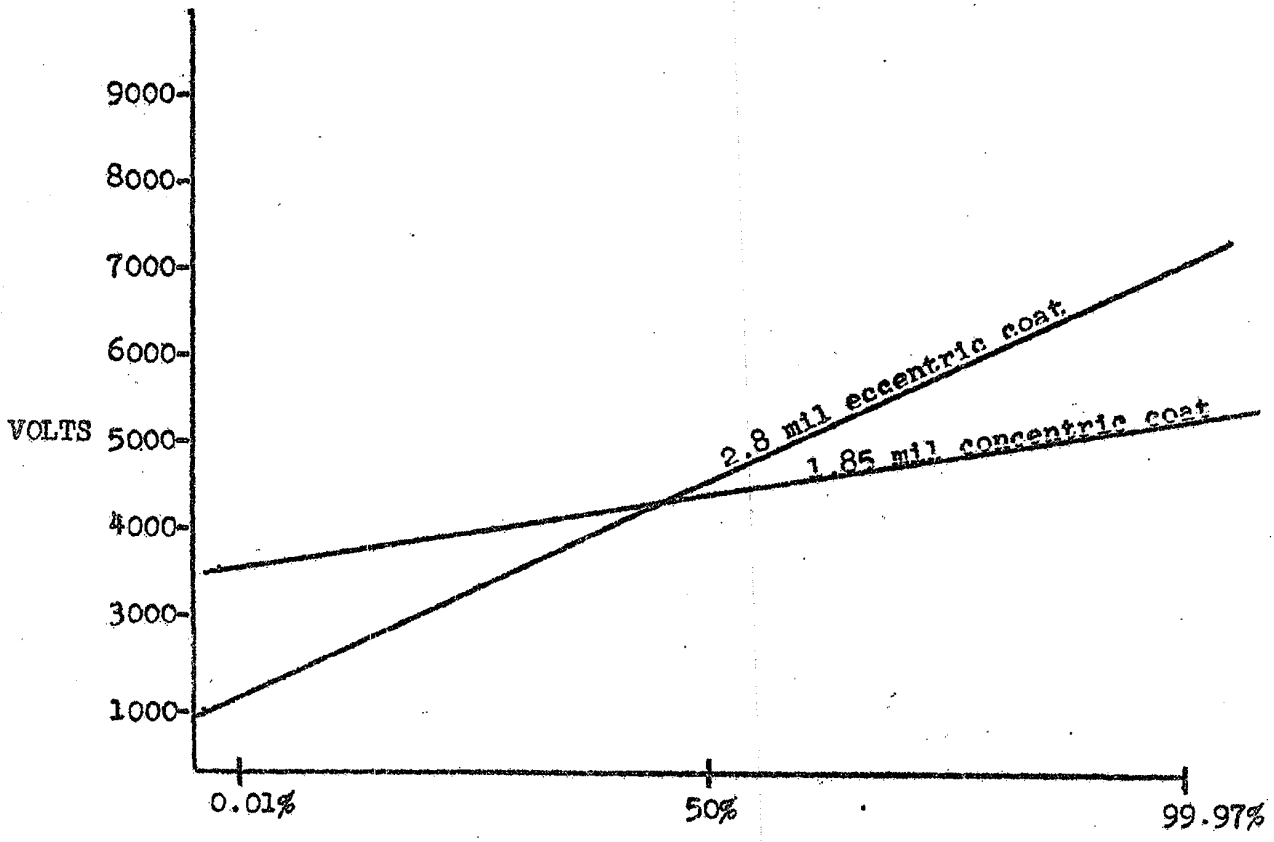


TABLE IV

EFFECT OF EXPOSURE ON MECHANICAL PROPERTIES OF ALKYDS

ALKYD CODE	TENSILE STR.	ELONGATION	TOUGHNESS	LOSS IN TOUGHNESS %		
				HEAT (a)	UV(b)	WEATHEROMETER (c)
1	2500	99.5	1250	34	97	91
2	2900	68	1000	27	100	91
3	3100	59	930	37	98	90
4	3100	80	1265	Gain 8	94	70
5	3400	66	1120	22	99	79
6	3000	51	777	6	85	6
7	2500	33	419	42	100	70
8	330	40	650	100	100	100

(a) 140°F. 100 hrs.

(b) 100 hours Fadeometer

(c) 120 hours Weatherometer

"Electrical Properties of Organic Films"
by Dr. T. W. Dakin, Westinghouse Research Lab., East Pittsburgh, Pa.

In the use of films for electrical purposes three properties are considered of outstanding interest:

1. Conductivity D.C. and A.C.
2. Dielectric constant
3. Dielectric strength.

Films used for electrical purposes are assumed to be very viscous liquids. They are considered as solvents of low dielectric constant, ϵ'. As a result of the low dielectric constant, ions are only slightly soluble in the film. In addition, ionizing materials have a low dissociation constant. The dissociation constant is given approximately by the expression:

$$- \log K_D = K/\epsilon'$$

Conductivity of films indicated by the symbol σ is of the order 10^{-10} to 10^{-16} ohms^{-1}cm. The conductivity is assumed to vary approximately inversely to the viscosity or hardness. In films, salts are the greatest contributors to the conductivity. Acetic acid and other carboxylic acids yield extremely low conductivities.

The observed conductivity is made up of contributions from various sources. Incidental quantities of water may result in materials of enhanced conductivity to D.C. and A.C.. Ions increase conductivity to D.C. & A.C. Dipoles affect only the A.C. conductivity, but their effect is quite pronounced at certain frequencies. The response of organic films to alternating currents is characterized by a relaxation time τ. When the frequency of the applied A.C. is of the same order as the relaxation time, then profound effects are noted in the dielectric constant and in the dielectric loss. To study the relaxation time measurements of dielectric constant and dielectric loss therefore are made as a function of frequency. In measurements of relaxation time of polymers it has generally been found that the relaxation time increases as the molecular weight of the polymer increases.

Measurements have been made of the loss in a linseed oil glycerol phthalate resin at various temperatures. At 75°C. the loss has a peak at 10^{-4} cycles per second; at 50°C. at approximately 400 cycles per second; at room temperature the peak is below 0.1 per sec. This sort of information has its parallel in the mechanical behavior of the films. It is well established that certain films will follow a slow mechanical deformation but will not follow a rapid one. It would seem that when films have a rapid relaxation time, then they can follow slow impulses without rupture but if they have a very slow relaxation time, then strain builds up rapidly in a stressed film and the films appear to be more brittle. The advantage of an electrical relaxation time test as compared with the mechanical relaxation time test is that in the process the film is not broken or permanently deformed. Repeated measurements can be made on the same film.

Dakin made the statement "dielectric breakdown is something we really don't know how to measure".... However, he pointed out several important aspects of making the measurements of dielectric breakdown. A prime cause of dielectric breakdown is corona, which erodes the film. This is a function of time.

Probably the major cause of difficulty with measurement of breakdown is that the defects are statistically distributed in the film. Figure 2 shows a typical probability distribution curve obtained from measurements of breakdown voltage on two coated wires. When longer samples of wire are used the probability of breakdown increases and the voltages therefore that would appear on this type of graph would be lower at equal percent probability. Dakin pointed out that, as a practical consequence, only very small voltages can be used in wires having extremely high breakdown voltages.

"Studies of the Mechanism of Crater Formation in Baked Surface Coatings" by S. Gusman, Rohm & Haas, Philadelphia, Pa.

When alkyd-UF films are baked craters generally form in the film. These have been traced to droplets of silicone for the most part. Even where extreme care is used to insure freedom from silicone contamination craters nevertheless are still formed but they are very much reduced in frequency. Gusman studied the statistical distribution of craters in films and made studies to determine how they could be reduced. He proved that crater formation generally occurs in the oven and is due to a reduction in the viscosity of the film prior to the cross-linking reaction. This viscosity reduction is, of course, due to the high temperature in the oven. Gusman worked out an interesting technique for following the viscosity of a film while it was in the oven. He built up a thick film and then observed some small defect or dust particle in the surface as it flowed down with the panel in the vertical position. He followed this flow by means of a cathetometer. It is interesting to note that the use of certain soluble silicones added to the U-F alkyd mixture reduced the formation of craters due to silicones. Anybody interested in following this problem further might communicate with Gusman at Rohm & Haas. He indicated that he would be happy to discuss with them all his findings on that subject that were made public at the conference.

"Theories of Adhesion"
by S. W. Reinhart, U.S. Bureau of Standards, Washington, D.C.

Reinhart admitted that all of the instruments that are now in use for measuring adhesion measure some complex quantities that are only slightly related to the true specific adhesion. The best overall instrument, he believes, is the Interchemical Adherometer, which measures a variety of factors. There is reason to believe, however, that in many cases the Interchemical Adherometer gives results that are at variance to what other logical considerations would lead one to believe. Among the factors contributing to adhesion is an interesting one - the relation between the thermal coefficient of expansion of the coating and that of the substrate. He described a study which indicated that in order to obtain satisfactory adhesion of a primer to a substrate it was necessary to make the thermal coefficients identical by the use of selected extenders

in carefully adjusted amounts. He believes that, in some cases, this is the most important determining property. (Bureau of Standards Research Paper 1745 - Oct. 1946 by Philip S. Tuner.)

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