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Vinyl Plastisol and Organosol Coatings for Paper

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The use of vinyl plastisols and organsols as coatings for cloth, paper, and flooring substrates has grown to be a substantial portion of several industries. This paper summarizes the technology involved in the use of these liquid vinyl systems and includes a discussion of the basic components of a vinyl compound; its room temperature rheology; its changes in rheology as it proceeds to gelation; and its ultimate development of useful physical properties as it is fused with heat. Compounding and application techniques are also covered.

Keywords: Webs paper · Cloth · Fabrics · Organosols · Coatings · Dispersions · Plastisols · Vinyl resins · Viscosity · Temperature · Physical properties

MANY familiar products in the home and in industry are fabricated from vinyl plastics or use vinyl in their construction in combination with other materials. Some of these are listed in Table I.

The bulk of vinyl plastics is processed through heavy duty equipment such as Banbury mills, two roll mills, extruders, calenders, injection molders, etc. This equipment must be powerful to knead the various components of a vinyl plastic together into a homogenous state. This equipment is necessarily quite expensive. In each case considerable heat is required to bring the vinyl to a thermoplastic state so that it can be squeezed or molded into a useful shape.

However, a technique is available that utilizes the various components of a vinyl plastic in such a way that a fluid material is formed at room temperature. These fluid vinyl systems are known as plastisols and organosols.

COMPONENT PARTS OF VINYL PLASTIC

The basic vinyl formulation consists of two major components, the vinyl polymer itself and a softening agent (plasticizer), which when fluxed with the vinyl polymer acts to separate the polymer chains. The amount of plasticizer present controls the hardness and rigidity of the product.

Vinyl polymer are of two types: straight PVC (polyvinyl chloride) homopolymers and copolymers, in which vinyl chloride is copolymerized with several other comonomers such as vinyl acetate, vinyl maleate, and others. The level of comonomer may go as high as 15% in the plastic grades of vinyl resin.

Vinyl plastics are formulated into products varying in hardness from very hard, such as pipe, conduit, home siding, credit cards, to very soft products, such as dolls, toys, and stocks used for upholstery and clothing. In the former instance little or no plasticizer is present. In the latter instance quantities of plasticiser equal to the weight of the PVC resin itself are used.

Vinyl plastics are processed at elevated temperatures to take advantage of their thermoplastic nature in forming them into useful shapes and a considerable exposure to heat is involved. Without some chemical assistance, the vinyl polymer itself would rapidly darken and decompose. Fortunately there are many stabilizing materials available that work well with vinyl in maintaining its thermal stability. These are organic compounds based principally on barium, cadmium, zinc, and lead. As each metal serves a special stabilizing function, a balanced stabilizer system contains two or more of them.

As in other products, pigments are used for coloration and fillers are used for cost reduction. When a cellular product is needed, any one of a number of chemical blowing agents is employed. Of course there are many other specialty materials used with this combination of PVC polymer, plasticizer, stabilizer, etc., each providing many essential processing and application features.

PLASTISOLS FROM VINYL DISPERSION RESINS

A form of vinyl resin is available such that when simply mixed with the liquid plasticizer a stable fluid or paste is formed. Here, the vinyl resin particles are uniformly distributed throughout the continuous plasticizer phase much like particles in a latex. The vinyl particles are sufficiently fine to do this, e.g., 0.2 to 3 microns. They do not settle out and such mixture remains stable almost indefinitely.

The other vinyl components such as fillers, stabilizers, pigments, etc., are similarly included in the formulation. Liquids such as stabilizers are dissolved in the plasticizer. Pigments, fillers, etc., are dispersed in it, as is the resin. As expected, a soft vinyl plastic resulting from a high plasticizer level will be more fluid than a harder product with less plasticizer available to dilute the continuous liquid phase. Under sufficient magnification the vinyl resin particles can be seen to be uniformly dispersed in the plasticizer phase as schematically shown in Fig. 1.

PROPERTIES OF PLASTISOLS

Gelation and Fusion

After a plastisol is coated onto a substrate, molded into a useful shape, or

Table I. Applications of Vinyl

Production	*Construction*	*Fabrication technique*
	In the home	
Shower curtains	Unsupported film	Calender
Table cloths	Film, unsupported or supported on cloth	Calender or spread coated
Flooring	Film and/or foam on felt or asbestos	Spread coated
Clothing (jackets, handbags, hats, shoes, belts)	Film and/or foam, unsupported and supported on cloth	Calender and spread coated
Dolls and toys	Hollow moldings	Slush and rotationally molded
Pipes, rain gutters, window channels	Rigid	Extrusion
	In industry	
Conveyor belts	Plies of vinyl on cloth	Spread coating and press lamination
Electrical wiring	Vinyl coated on wire	Extrusion
Ducts	Vinyl coated onto duct work	Spraying

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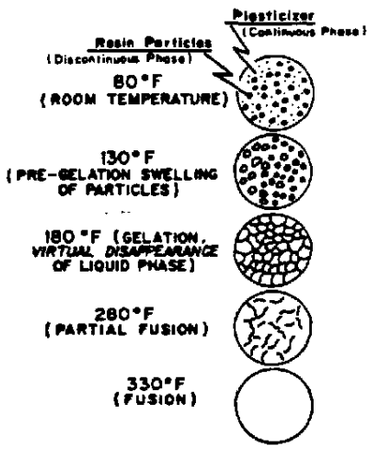
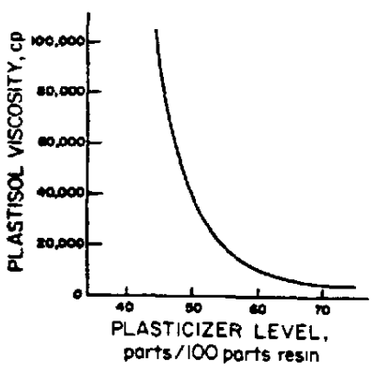


Fig. 1. Plastisol gelation and fusion; temperatures shown vary with each specific formulation.



Test recipe: Marvinol 50—100; DOP—as shown

Fig. 2. Plastisol viscosity vs. plasticizer level

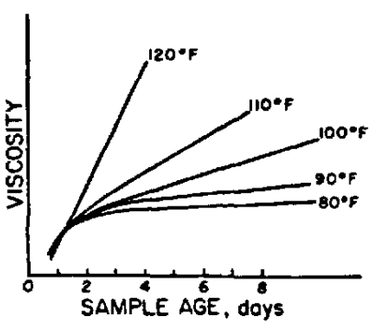


Fig. 3. Plastisol viscosity stability vs. storage temperature

fabricated in some other way, heat is applied to convert it into its solid state. This is called fusion. Although the fusion process takes but a minute or two in the usual industrial applications of a vinyl plastisol, a number of changes take place in the physical state of the material during this brief interval. The plastisol is heated in a convection oven, or by a bank of infrared lamps, or in a high-frequency induction system. This causes the plasticizer to soften the vinyl resin particles, swelling them, until finally each swollen particle touches its neighbor (Fig. 1). At this point most or all of the plasticizer has been absorbed by the resin particles; the plastic is dry, but it has virtually no physical strength. This is called the gel stage. It is a useful phenomenon in certain types of vinyl plastisol processing where the coating thickness of a dipped or molded vinyl is controlled in this fashion. Gelation temperatures vary with formulation, but most fall within the 150–200°F range.

As heat continues to penetrate the system, the PVC particles lose their identity, as such, as the plasticizer begins to separate the polymer chains. Now the polymer chains are in a sense dissolved in the plasticizer. This is fusion. Although varying with formulation, fusion generally starts in the 280–300°F range, with complete fusion developing at 325–350°F. On cooling, the plastic is characterized by useful tensile strength, abrasion and chemical resistance, plus all the other attributes associated with vinyl coatings.

Viscosity at Room Temperature

A plastisol may be held at room temperature for a relatively long period of time before it is processed through a pump and applied to some substrate by a roller or knife coater. Hence, its room temperature viscosity properties merit considerable attention.

Figure 2 describes the viscosity of a plastisol at varying levels of plasticizer. As plasticizer is withdrawn from the system, viscosity increases. At first this viscosity change is slight, but it increases rapidly at the lower plasticizer levels. When attempting to apply a low plasticizer level compound, its viscosity may be well above a coatable level. In such an instance, it is necessary to dilute the plasticizer with a volatile diluent that will reduce compound viscosity, yet flash off during fusion to maintain the proper PVC/plasticizer ratio in the fused composition. Such systems are known as organosols and will be covered in greater detail later.

Although plastisols are quite stable in their liquid state, exposure to a slightly elevated temperature will cause partial gelation of the compound, manifesting itself in a gradual viscosity increase. The magnitude of this increase is dependent on storage temperature as depicted in Fig. 3. This strongly suggests that care should be exercised in maintaining proper storage conditions in the day-to-day handling of plastisol compounds. A maximum ambient storage temperature of 90°F is recommended, although some exposure to higher temperatures for short periods will not be harmful.

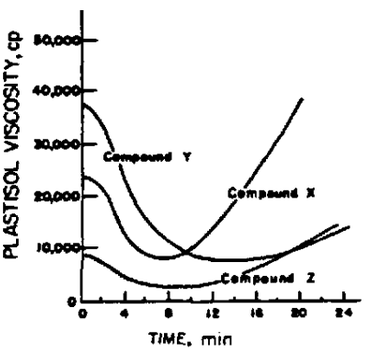


Fig. 4. Pre-gelation viscosity. Bath temperature 150°F

Pre-Gelation Viscosity

A plastisol is generally exposed to fusion temperatures for a period of 1–2 min in most industrial applications. Thus, the amount of time in the so-called pre-gelation temperature range, i.e., between room temperature and gelation, is relatively short, perhaps $^1/_2$ min or less, depending on formulation, fusion conditions, etc. The viscosity properties of a plastisol in this pre-gelation temperature zone are quite different from its properties at room temperature.

Figure 4 plots the viscosity of three compounds as a function of time. The time interval here is deliberately made longer than actually experienced during fusion as noted above, so that the changes in viscosity that occur can be examined in greater detail. This is done by exposing the plastisol to temperatures considerably lower than full fusion conditions but sufficiently high to bring the plastisol through its pre-gelation stage as shown.

These changes in viscosity are particularly important in cloth coating work where the reduced viscosity of a plastisol during pre-gelation may cause the compound to strike through the interstitial spaces in the cloth. This temporary viscosity reduction is generally not a problem when the substrate is not porous.

Fusion Temperatures

As already described, the vinyl must be fused to develop useful properties. Although a semblance of fusion may be detected at temperatures as low as 280°F for standard formulations, useful properties do not develop until about 325°F. Figure 5 describes the temperature-time-tensile strength relationship for an organosol compound with 35 parts of plasticizer per 100 parts of resin (abbreviated 35 phr). With oven air at 350° and 375°F, the time to accomplish fusion is reduced. The higher tensile values noted at 400°F result from a loss of plasticizer from the film as a result of this exposure to excessive temperature.

Copolymer resins and solvating plasticizers, e.g., tricresyl phosphate, will shift these curves downward with fusion developing in the 250–300°F range. The ultimate physical strength developed by copolymer resins is less than that developed by homopolymers, when each is fused at its respective optimum fusion temperature. Where oven heat capacities are limited or heat sensitive substrates are being coated, copolymer resins do provide higher strength values at lower temperatures. Where sufficient oven capacity is available, standard PVC homopolymers and standard plasticizers, e.g. dioctyl phthalate (DOP), are used.

ORGANOSOLS

Because the plasticizer level of a plastisol compound is determined by the end product requirement, the resultant plastisol viscosity is often not ideal for ready application. In such cases, adjustments are made with various formulating ingredients to develop the required rheological properties. A spray or cold dip plastisol is a typical example. Here sufficient plasticizer is generally available in the formulation to provide a fluid paste. However, the need for low viscosity and high yield value, required for the proper application of the compound, is met by adjusting viscosity with high oil absorptive fillers or gels and volatile diluents.

In other cases, the need for hardness or rigidity in a product may call for a reduction in the plasticizer level, below which a sufficiently fluid paste may not be formed. Here adjustment with a small amount of volatile diluent is adequate to develop enough fluidity for application. The volatile diluent is evaporated during fusion. Such formulations, generally referred to as modified plastisols, are commonly used in fabric coating and rotational molding of rigid type plastisols.

When the plasticizer level has been reduced to the point where it is difficult or impossible to form a paste when mixed with resin, volatile diluents are used in the initial mixing of the compound. These compounds are known as organosols.

Diluent Selection

Volatile solvents and diluents, such as ketones and aromatic and aliphatic hydrocarbons, are commonly used to dissolve and disperse vinyls. Ketones are good solvents for solution grade vinyls and have a strong solvating effect on dispersion grade PVC resins. Consequently, if they were used as the sole diluent in organosols, high viscosity and poor viscosity stability would result. The aromatic hydrocarbons, although nonsolvents for PVC, have a partial solvating or swelling effect on dispersion resin intermediate to that of the ketones and aliphatics.

Aliphatic hydrocarbons, known in the paint field as petroleum naphthas, are actually mixtures of paraffins, naphthenes, and aromatics. These materials are available in a wide variety of boiling ranges and aromatic-aliphatic content. Their ability to dilute the plasticizer and thereby lower the viscosity of the continuous phase without solvating or swelling the PVC resin particles makes the aliphatic type naphtha particularly useful in this work.

The way in which the viscosity of an organosol is brought into a useful range is shown in Table II. Here a plasticizer level of 25 parts per 100 parts resin is required for a hypothetical paper coating application. Ten parts of diluent are needed for the initial mixing of the compound (Recipe A). Attempts to coat this formulation resulted in excessive force being required for the high speed coating of the paper and poor flow-out of flow lines that developed in the coating. The high high-shear and high low-shear viscosity of this compound correlate with these two observed flow phenomenon, respectively. An adjustment with three additional parts of diluent brought both the high- and low-shear viscosity down, as noted in the data (Recipe B). The compound then coated satisfactorily but still flowed out poorly. The high-shear viscosity was then adequately adjusted. A further adjustment in the low shear range was needed to eliminate the flow lines. The use of additional quantities of diluent may result in excessive fire hazard or the development of diluent blisters due to trapped naphtha in the film during fusion. Therefore an alternate means of viscosity adjustment was used. A nonionic surfactant added to the compound brought its low shear viscosity to a satisfactory level. This addition did not significantly alter the high-shear viscosity. This compound, altered by the addition of naphtha diluent to adjust high-shear viscosity and wetting agent to adjust low-shear viscosity, provides a properly formulated organosol compound for high-speed paper coating.

Special polymeric plasticizers may sometimes be used in a plastisol or organosol formulation to provide special properties, such as extraction resistance, in a vinyl film. These plasticizers are not soluble in aliphatic naphthas. Consequently there have been instances

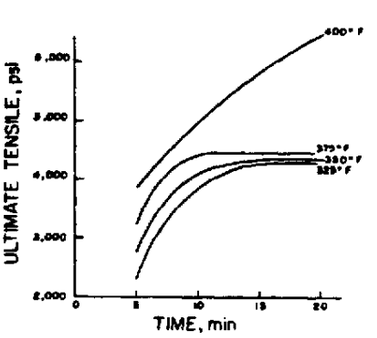


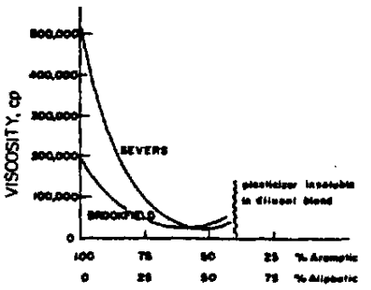
Fig. 5. Plastisol fusion properties; plasticizer level—35 parts per 100 parts resin (phr).

Table II. Viscosity Adjustment of an Organosol

	A	B	C
		Formulation	
PVC dispersion grade resin	100	100	100
Plasticizer	25	25	25
Stabilizer	3	3	3
Diluent—aliphatic naphtha	10	13	13
Wetting agent—PEG400DO			1.4
		Viscosity, cps	
Brookfield (low shear)	21,800	10,700	2,900
Severs (high shear)	31,500	11,800	9,800
		Coating properties	
Drag resistance	High	Low	Low
Flow-out	Poor	Poor	Good

where adding naphtha diluent to such compounds raised viscosity. It is therefore necessary to develop useful diluent systems for such compounds.

Figure 6 describes the high- and low-shear viscosity properties of a polymer plasticiser-based compound using blends of aliphatic and aromatic hydrocarbon diluents. An all-aromatic diluent produces a very dilatant compound, i.e., its high shear viscosity is many times its viscosity at low shear. A 50:50 blend appears optimum for low viscosity but is close to the insolubility point. From such a plot, a 60:40 aromatic:aliphatic blend appears useful.



Test recipe: Marvinol 50—100, Paraplex G54—50, diluent blend—25

Fig. 6. Organosol diluent blend.

Rheology of Plastisols and Organosols

Because plastisols and organosols are liquid systems and are applied as such, their application performance is inextricably tied to their rheological properties. A comprehensive knowledge of this subject is essential to the plastisol and organosol user. However, it is beyond the scope of this paper to discuss this in detail, and only a few fundamental concepts will be presented.

First, unlike water, oil, and other common fluids, the vinyl systems described above are non-Newtonian, i.e., their viscosity is a changing function dependent on the shearing action and time associated with their application. If their viscosity increases with increasing shear, they are "dilatant"—an undesirable feature. If some force must be overcome before flow will occur, the material exhibits "plastic flow." The initial force necessary to initiate flow is called "yield value." If the viscosity of a compound is observed to decrease as a function of time, "thixotropy" is evident.

There are other flow phenomena to be observed in these systems, but these are the essential ones. If we were to measure some of these properties in a single sample, as we frequently do using a rotational viscometer, a rheogram, as shown in Fig. 7, may be constructed from these data. A rheogram plots shear stress, as measured by the deflection of the viscometer spindle, against shear rate as measured by the rate of rotation of the viscometer cup. These are plotted on the Y and X axes, respectively. The lower values of downcurve shear stress compared with upcurve data indicate the thixotropic nature of the compound. The finite value of shear stress at zero shear rate represents yield value.

Viscosity *per se*, or more accurately apparent viscosity, is represented by the slope of the line connecting the origin with any point on the curve. The two viscosity lines shown indicate the dilatant state of the compound, i.e., the higher viscosity associated with the higher rate of rotation.

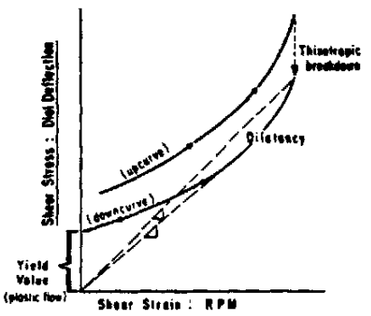


Fig. 7. Rheogram of a plastisol.

Foamed Vinyls

Up to this point the discussion of vinyl coatings on paper has been restricted to a consideration of solid coatings, both clear and pigmented. Foamed vinyl coatings on cloth have become so popular in recent years for clothing and upholstery that their use on paper should be considered as well.

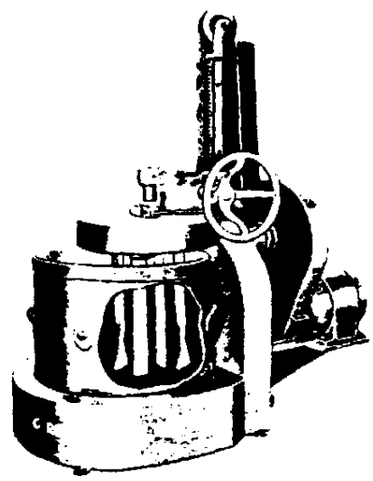


Fig. 8. Slow speed change can-type mixer (photo courtesy C. Ross & Son Co.).

Vinyl foam coatings may be produced by whipping air into specially formulated plastisol compounds. Vinyl foam is also produced by incorporating chemical blowing agents into the compound. In the former technique, air is mechanically whipped into a plastisol, compounded with a wetting agent so that the resultant froth is reasonably stable. This froth is spread onto a substrate and passed through a fusion oven. Because it is difficult to force heat throught a foamed structure, the thickness of foam must be maintained at a relatively low, but nevertheless useful, level. Foam thickness in this case may be increased by using the more sophisticated induction heating techniques for plastisol fusion. This type of foam is open cell in nature, i.e., the cells connect with one another. Also, it is restricted to the softer stocks because a relatively high plasticizer level is required to maintain the low viscosities needed for adequate frothing of the compound.

Most vinyl foam is manufactured using chemical blowing agents in vinyl plastisols. The use of azodicarbonamide far outweighs the use of other blowing agents in this application.

Here is a typical starting point formulation for such a product:

PVC[1] resin	100
DOP	95
Epoxy plasticizer	5
Azodicarbonamide	3
Stabilizer	3

The use of a medium molecular weight resin is preferred. Activation of the blowing agent occurs at relatively high temperatures, i.e., 325–350°F. At this point the vinyl is in its fluxed, hot-melt state. The medium molecular weight resin provides a less viscous hot-melt plastic, which is capable of more readily expanding into a fine cell structured foam under the influence of the activated blowing agent. Through compounding and fusion temperature techniques, it is possible to control the density of the foam, cell size, and the degree of porosity.

Plastisol Compounding Techniques

The relative ease with which plastisol resin may be blended with plasticizers and other formulating ingredients partially accounts for the rapid growth of this field. Consequently, a brief discussion of the various mixing techniques available is in order.

For the bulk of plastisol and organosol work, the Change Can or Pony type mixer is quite adequate (Fig. 8). A normal mixing cycle would involve charging the mixer with sufficient plas-

[1] A medium molecular weight PVC dispersion grade resin.

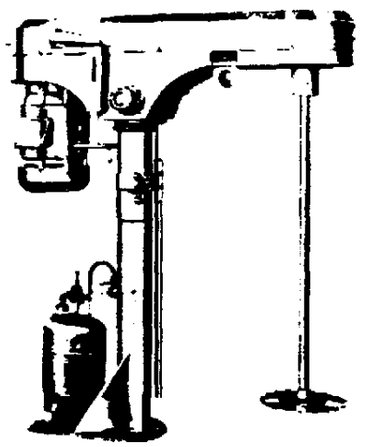


Fig. 9. High speed mixer (photo courtesy Morehouse-Cowles Co.).

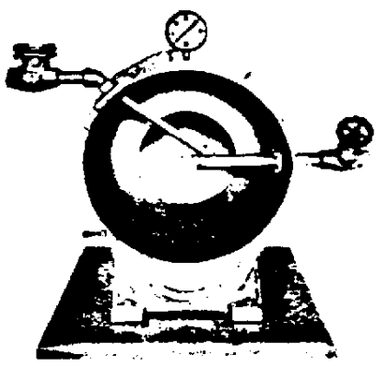


Fig. 10. A deaerator (photo courtesy Cornell Machine Works, Inc.).

ticizer, or in the case of an organosol, plasticizer and diluent, to wet the resin into a fairly heavy paste, thus permitting effective transmission of shear forces throughout the mix. When all the resin has been thoroughly masticated, the balance of the plasticizer or diluent and other formulating ingredients can then be blended in slowly. From this point the batch may be further processed through paint mills and deaerators, if necessary. This mixing technique may be satisfactorily applied to most types of plastisol and organosol compounds.

In the manufacture of organosols and plastisols of the low-viscosity type, it is possible to utilize another type of mixer that eliminates the necessity of keeping the paste in a heavy stage for effective mixing. This mixer, shown in Fig. 9, operates at very high speeds.

Because the high-shear mixing action takes place in the immediate vicinity of the rotating blade, it is necessary to have rapid circulation of the compound to prevent localized overheating and consequent gelation of the material, thus requiring compounds with low viscosity properties. Consequently, all the liquid ingredients are first blended in the mixer, after which the resin is added in increments.

Ball and pebble mills used extensively in the paint field are frequently used to compound plastisols and organosols. Because no real grinding action is required, only a deagglomeration of the soft resin clusters, considerably more latitude with respect to ball or pebble charges and compound loading may be tolerated than with paints. Frequently deaeration can be accomplished in the same mill by rigging it for vacuum.

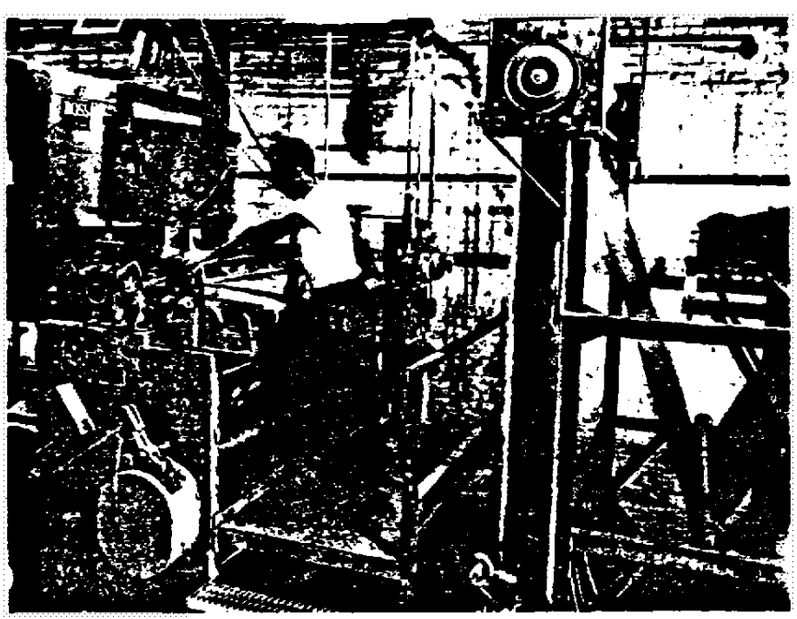


Fig. 11. Knife over roll coater (photo courtesy J. Waldron Co.).

Fig. 12. Reverse roll coater (photo courtesy Bonded Fibers Co.).

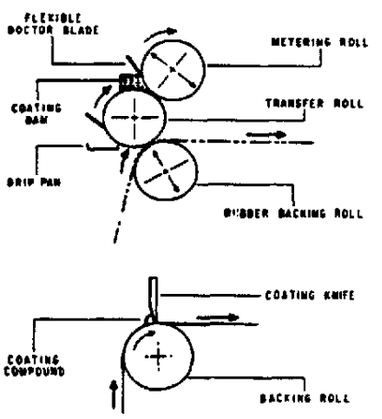


Fig. 13. Schematic drawing of reverse roll and knife coater (based on drawings by J. Waldron Co.).

Occasionally, an operation cannot tolerate the presence of any undispersed resin agglomerates in the finished compound. In such instances a single, loose pass through a three-roll paint mill is sufficient to disperse any resin clusters that may remain undispersed in the compound. When deaeration is necessary, any one of a variety of vacuum setups may be used. Figure 10 illustrates a commercial apparatus available for this purpose.

COATING TECHNIQUE

Basically two types of coating equipment are employed in coating paper and cloth substrates. These are knife over roll and reverse roll coaters, both high-shear devices, as shown in Figs. 11 and 12. Figure 13 shows these devices schematically.

In knife coating, the compound is metered onto the paper by controlling

the gap setting or clearance between the knife edge and the backing roll. In reverse roll coating, the plastisol is first metered between two rolls before transferring to the paper. This latter technique provides accurate coating weights down to about 3 mils.

After coating, the plastisol is fused in a conventional forced air convection oven. Although infrared radiation is occasionally used, it does not provide the uniform and reasonably close temperature control needed to prevent either under- or over-fusion of the compound. Under-fusion of the plastisol or organosol will result in a relatively weak film. Overexposure to heat may result in thermal degradation of the substrate and/or vinyl compound as well as volatilization of some plasticizer from the cast film with its subsequent change in the designed physical properties of the film.

Blending Resins

Up to this point the discussion has dealt with plastisols and organosol systems that are based on the fine particle size plastisol or dispersion grade PVC and copolymer resins. There is another type of PVC resin that has recently found a place in this type of work, known as plastisol blending resin.

The major distinguishing characteristic of a blending resin is its particle size, which is many times the particle size of a dispersion grade resin, ranging between 5 and 75 μ and higher by comparison with the 1 μ size of a dispersion resin. Consequently, a blending resin is not capable of forming a paste with plasticizer, but it may be used in conjunction with the paste-forming dispersion resin. A 30–50% blend with dispersion resin is commonly used.

Blending resins are used in plastisol and organosol compounds primarily because they lower compound cost. They vary in cost, but are as much as 8¢/lb lower than dispersion grade resin. In a 50:50 blend, average resin cost may be reduced up to 17%.

The particle size determines the suitability of a compound in paper coating as well as in other spread coating applications. Because of the manner in which a plastisol is spread, i.e., through knife and reverse roll coaters, large particles tend to lodge in the coating nip and gouge out a long channel in the coated paper before slipping through. Consequently, blending resins for spread coating must be well regulated for particle size.

Blending resins vary in molecular weight. As with all PVC resins, the higher molecular weight blending resins provide higher physical strength by comparison with those polymerized to a lower molecular weight. When strength properties, such as tensile or tear, are an important consideration, it may be possible to compensate for the lower strength resulting from the use of a lower cost, lower molecular weight blending resin by reducing the plasticizer level somewhat. In such a case, however, the selection of a higher molecular weight blending resin is strongly indicated. Although such resins are generally more expensive, they still represent some saving compared with dispersion grade resins.

Blending resins also lower the gloss of a plastisol or organosol compound by virtue of their relatively large particle size. For many products, this feature is of considerable value.

CONCLUSION

Much has been said in this paper regarding vinyl dispersion resins and their use in plastisols and organosols with specific reference to their use as paper coatings. It is beyond the scope of this paper to develop the chemistry of vinyl resins, plasticizers, etc., or the use of vinyl resins other than the dispersion and blending resin grades. However, a proper understanding of this subject necessarily includes these as well as other facets of vinyl technology. Such subjects are commended to the reader for future study.

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