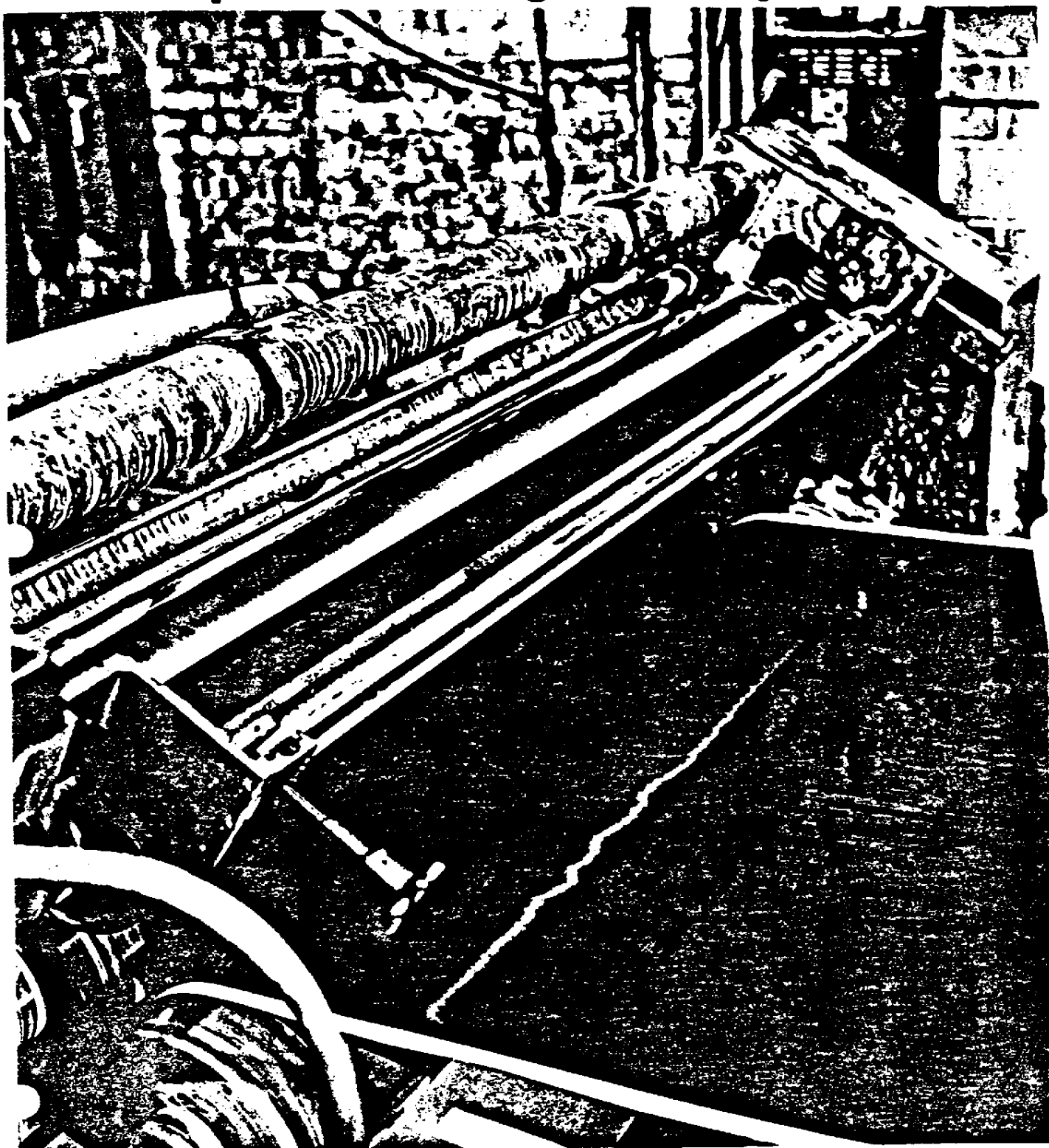


Marvinol 50, an all-purpose PVC plastisol and organosol dispersion resin.

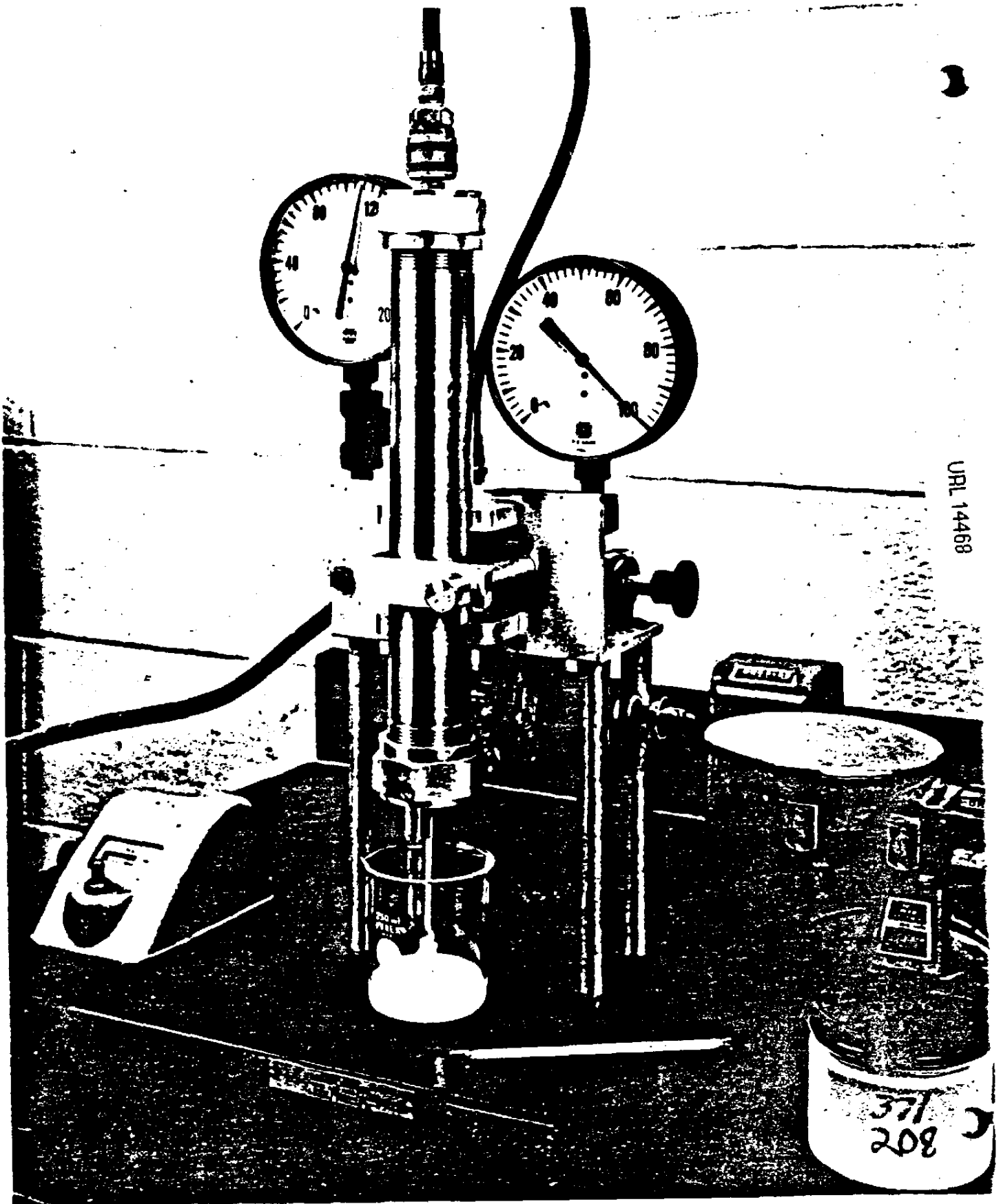


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Chemical Division

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Marvinol[®] 50 is ideal for a wide range of plastisol and organosol applications.

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Since the introduction of the PVC dispersion resin technique, many industries have utilized plastisols and organosols for the enhancement of their existing products and in the development of entirely new products. With the growth of these new products, it was inevitable that different types of vinyl dispersion resins would be made available with various end applications best served by specific resins.

Marvinol 50 is an all-purpose PVC plastisol and organosol dispersion resin developed by U.S. Rubber. It rapidly gained wide acceptance in the fabric, paper, and organosol coating fields where high and low-shear rheological properties are of such great importance.

Outstanding properties of Marvinol 50 include its controlled rheological properties at high and low rates

of shear, thus adapting it for a wide variety of molding, dipping, spreading and spraying applications. Its high gloss and clarity are ideal for many flooring and coated cloth products. Its high degree of taste and odor integrity makes Marvinol 50 very useful in food closure work. Marvinol 50 meets F.D.A. requirements for food contact applications.

Marvinol 50 is a homopolymer of vinyl chloride. Its typical resin characteristics are as follows:

Specific gravity	1.4
Specific viscosity*	0.50
Moisture and volatiles (max.)	0.4%
Apparent density	17 lbs/cubic feet
Methanol extract	1.3%

© U.S. Rubber registered tradename for its PVC resin.

*ASTM D-1243-60 Method B



Marvinol 50 can be supplied to meet your viscosity requirements.

Since dispersion resins by definition are processed as liquids at room temperatures, the ability of the resin to meet the rheological needs of the processor is of axiomatic importance.

Marvinol 50 can be supplied to meet a wide range of viscosity requirements.

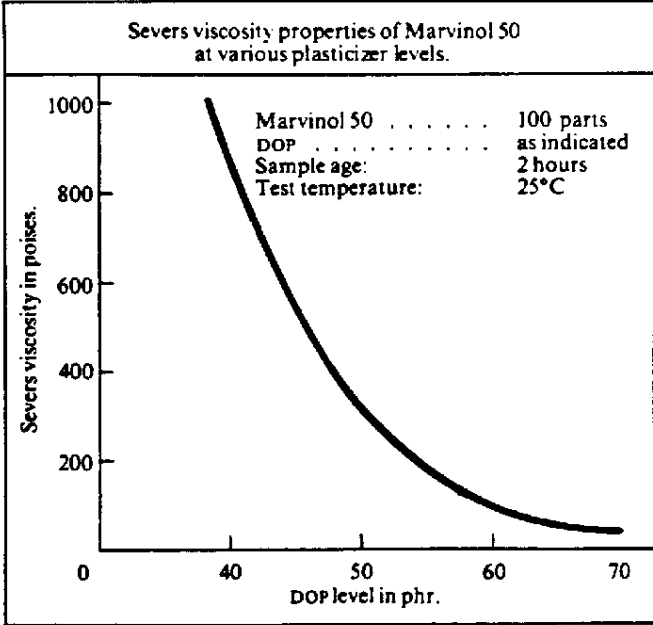
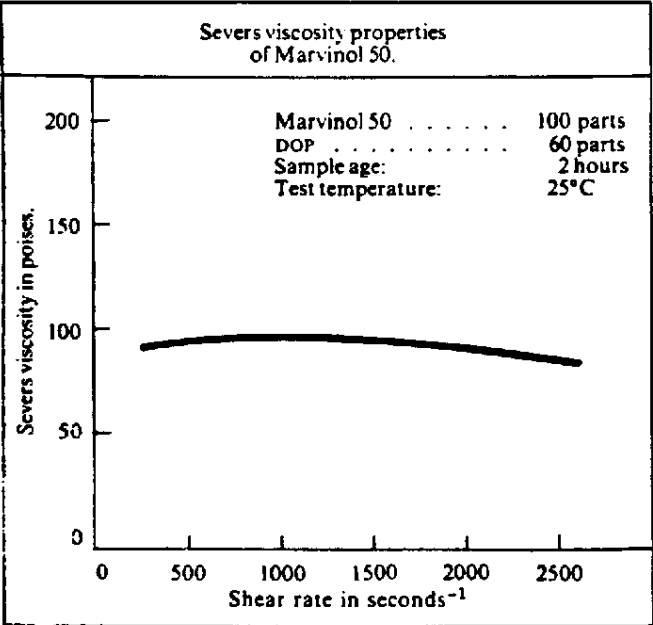
Because of the infinite number and widely divergent types of formulations in which dispersion resin may be used, it is a challenge to completely predict the performance of a resin from a single test recipe. However, experience has taught that in the high-shear rate coating of plastisols and organosols on cloth, paper, wire, glass yarn, etc., high-shear viscosity properties can be characterized by high-shear measurements made on a relatively simple plastisol formulation.

The diagram below is a plot of typical high-shear

viscosity properties for Marvinol 50. This curve illustrates the reason Marvinol 50 processes so well at high-shear rates. Low high-shear viscosities and the maintenance of Newtonian-like properties over a wide range of shear allow for rapid, dilatant-free coating.

The low high-shear viscosity properties of Marvinol 50 also enable the formulator to lower his plasticizer level without resorting to the organosol or modified plastisol techniques. This property assumes great importance in the casting of tough, low plasticizer level films at film thicknesses that preclude the use of volatile diluent.

The diagram below is a plot of Severs viscosity versus plasticizer concentration. This curve illustrates the unusually low plasticizer levels available to formulators using Marvinol 50.



How viscosity of Marvinol 50 varies with temperature and age.

One very important facet of high-shear rheology associated with plastisol formulations is the large viscosity response to changes in plastisol temperature. From the data in the diagram below (left) it can be seen that normal seasonal changes in ambient temperature will produce viscosity variations that could require formulating adjustments.

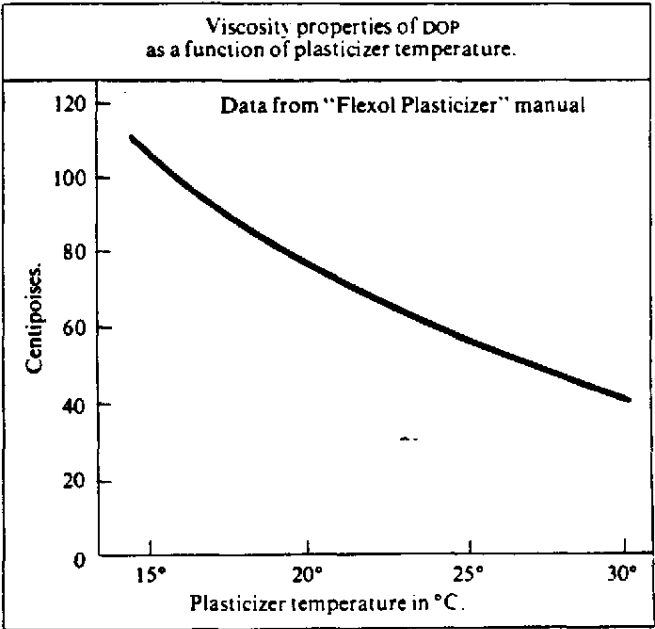
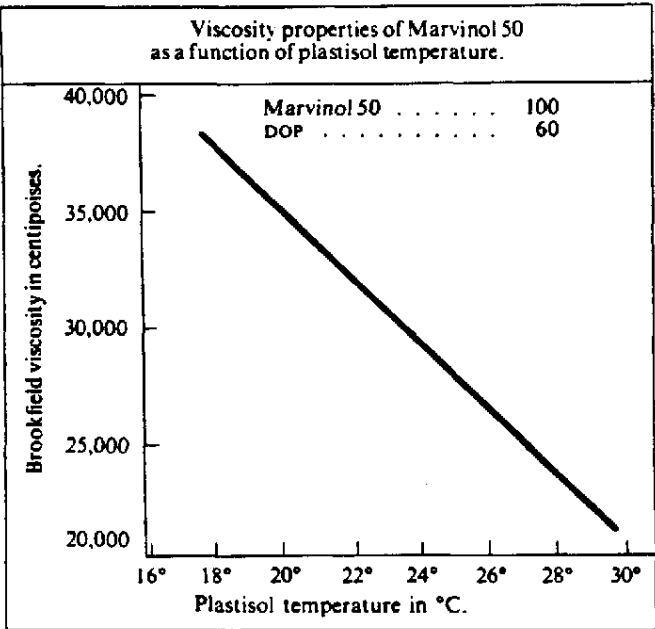
This viscosity variation is actually due to the change in plasticizer viscosity with temperature. Consequently, a study of the plasticizers used in a formulation

with respect to their viscosity-temperature relationship may become essential. These data are supplied in several plasticizer manuals. The viscosity-temperature data for DOP, a typical plasticizer, are shown in the diagram below.

In high-shear applications with only a few special exceptions low viscosity at high-shear is a desirable property.

With regard to a plastisol's low-shear properties, the preceding statement does not necessarily apply, i.e.,

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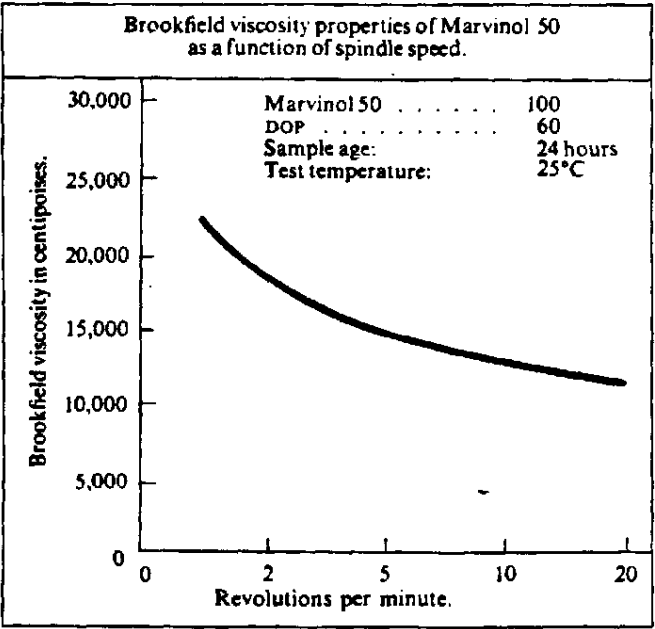
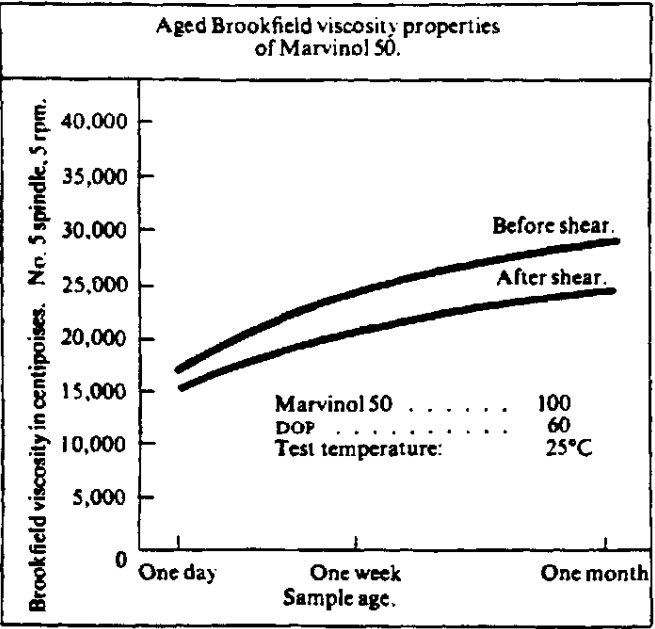
plastisols formulated for cold dipping or fabric coating would find too low a low-shear viscosity troublesome. Since many applications require unique low-shear viscosity properties, it is noteworthy that through the use of surfactants, gelling agents, and diluents basic low-shear properties of Marvinol 50 can be altered to a considerable extent.

The diagrams below illustrate the general type of low-shear properties associated with Marvinol 50 as measured with a Brookfield viscometer.

The diagram at left illustrates the normal increase in viscosity with age and how a share of this increase is due to thixotropic buildup.

The diagram at right illustrates the plastic and pseudoplastic nature of plastisols at low-shear. These flow properties are typical of many plastisol resins including those in the Marvinol series.

It is possible to supply Marvinol 50 resin for applications requiring a wide range of specialized viscosity properties.



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Marvinol 50 can be fused over a wide range of temperatures.

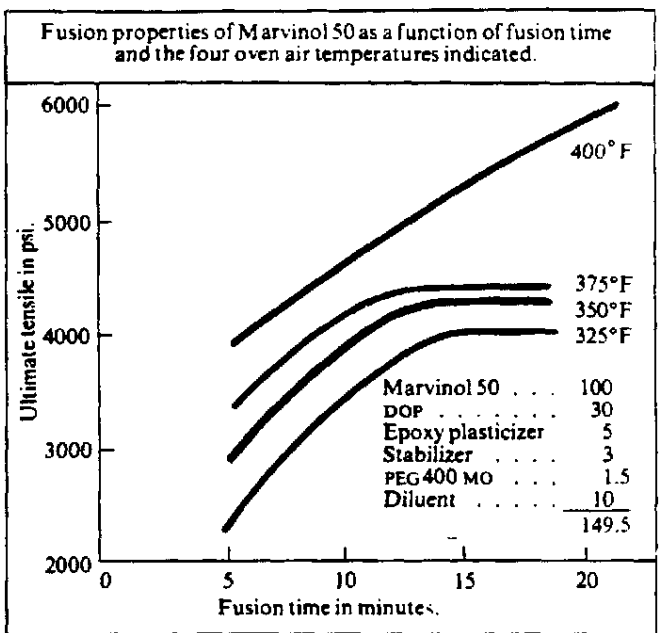
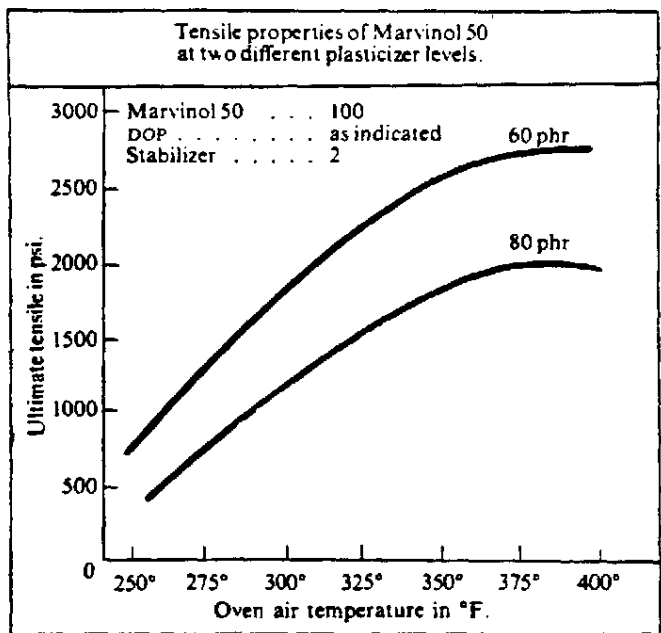
Once the plastisol is cast or applied, it is then necessary to fuse it into a useful product. This is done by exposing the plastisol to some suitable temperature in the 300°F to 400°F range and holding it there long enough to insure that the plastisol itself reaches its fusion temperature.

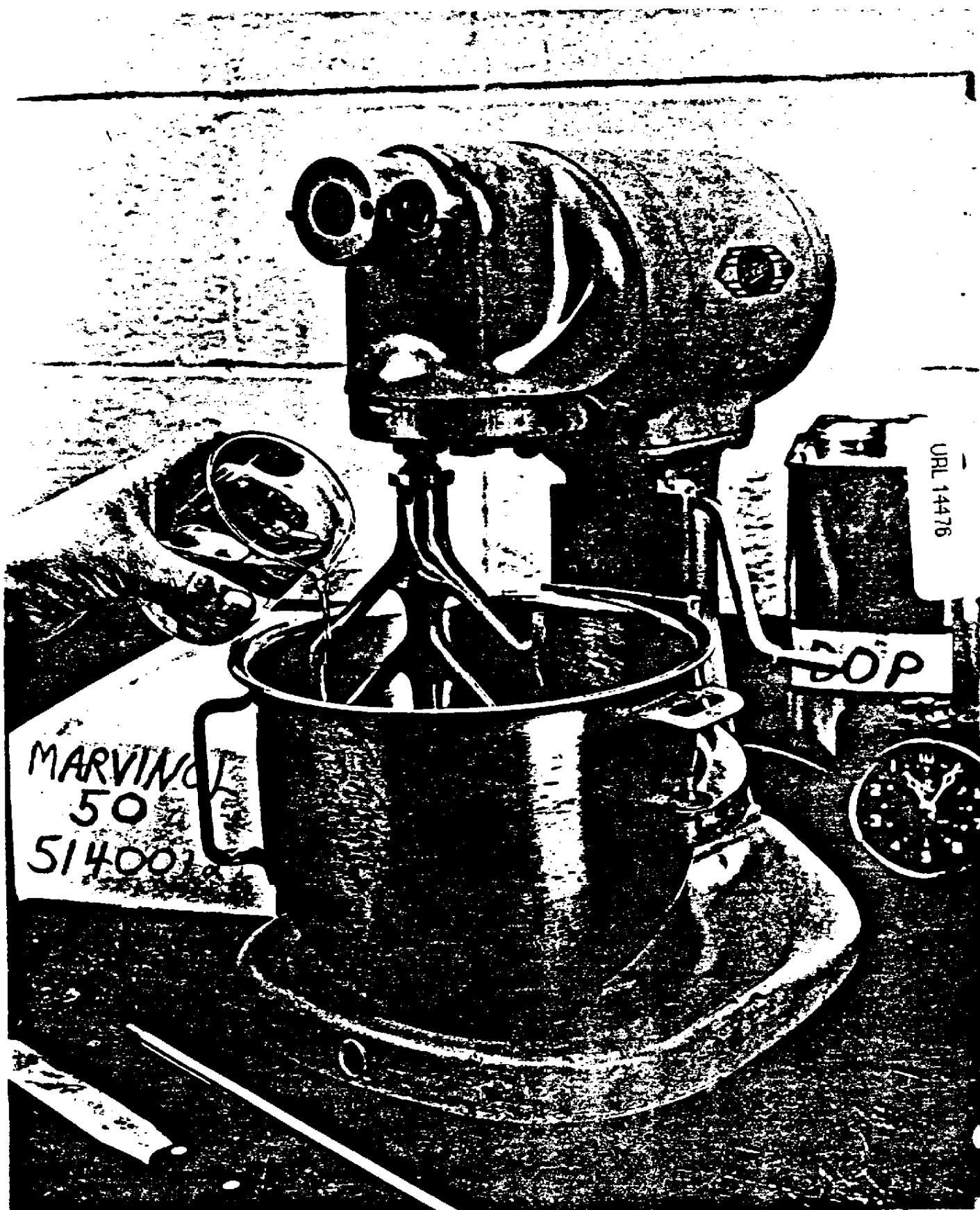
The diagram at lower left illustrates the development of a plastisol's fusion properties at two plasticizer levels as measured by ultimate tensile strength.

The diagram at lower right illustrates the development of an organosol's fusion properties as both a function of temperature and time. The reduced tensiles obtained at five minutes reveal that the films

have not yet reached the indicated oven air temperature and that for the particular oven involved approximately ten minutes is actually required. The continual increase in tensile at 400°F is the result of plasticizer volatilization from the film which is evidenced by a rapid weight loss of the film under these excessive fusion conditions.

Certain material or equipment limitations require reduced fusion temperatures, below the 325°F indicated by these data. In this event, the use of solvating plasticizers such as TCP is suggested. A comprehensive study covering "The Influence of Resin on Plastisol Fusion" is available on request.





Marvinol 50 is compatible with a wide range of compounding ingredients.

A single resin falls short of encompassing all the individual processor's detailed needs. For this reason U.S. Rubber has developed a family of dispersion grade resins where specific resins have been designed to meet specific requirements. A list of these resins is shown on page 16 and their use is described in the table of formulations on page 18.

The art of plastisol and organosol compounding may be put on a more scientific basis by the exercise of a few formulating principles. A typical recipe may consist of resin, plasticizers, stabilizers, a volatile diluent, fillers, pigments, and miscellaneous ingredients.

Here is a brief outline on the selection of the various components that go into a dispersion recipe:

Resins.

Dispersion type resins are homopolymers of PVC and copolymers of vinyl chloride with smaller amounts of comonomers. Resins vary in a number of important respects such as their non-PVC content, molecular weight, etc. The major difference between resins, however, is their ability to process in a satisfactory manner.

The following lists some of the major rheological plus other processing features the formulator is concerned with for some typical applications:

Fabric coating: (1) Low high-shear viscosity for ease of coating. (2) Medium low-shear viscosity for cloth penetration control.

Wire and yarn coating: (1) Low high-shear viscosity for ease of coating. (2) Medium low-shear viscosity for resistance to dripping prior to gelation and fusion.

Slush molding: (1) Low low-shear viscosity for good drainage. (2) Good air release. (3) Low gelation temperature for rapid buildup in mold. (4) Dry surface.

Rotational molding: (1) Low low-shear viscosity for uniform distribution in mold. (2) Good air release. (3) Medium-high gel temperature.

Organosols: (1) Low high-shear viscosity for ease of coating. (2) Low low-shear viscosity for good flow-out. (3) Compatibility with diluents. (4) High clarity and gloss.

Plasticizers.

Once a resin best suited to the end application has been selected, it must then be blended with plasticizers of the correct type and level. Blends of plasticizers will frequently impart the desired properties rather than one alone.

The following lists some general characteristics associated with each plasticizer type although not all the plasticizers in each group will actually possess these properties:

Phthlates: good compatibility, good balance of all properties (DOP, DIOP, DCP, DDP and mixed esters).

Phosphates: good flame resistance, reduced fusion temperature (TCP).

Polymeric: low extraction, high viscosity.

Epoxy (soybean type): enhances heat stability.

Epoxy (tallate type): enhances heat stability and low temperature flexibility.

Azelates, adipates: good low temperature flexibility, limited compatibility, low viscosity (DOZ, DOA).

Extenders: low cost, low viscosity, limited compatibility.

Although the resin generally imparts to the plastisol its basic rheological properties, the plasticizer is occasionally selected for its affect on viscosity. An example of this is the use of the low viscosity types for rigid plastisol molding work.

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(This discussion of compounding ingredients for Marvinol 50 is continued from the previous page.)

Stabilizers.

The stabilizer has the function of minimizing color development during fusion or any subsequent exposure to heat and light. This may be one of a number of proprietary lead, tin, barium, cadmium, or zinc compounds sold for this purpose.

The most widely used stabilizer systems in plastisol and organosol work are based on combinations of barium, cadmium and zinc compounds and are generally sold as a single blend. It is important to remember that it is always necessary to include a small amount of epoxy, generally epoxy plasticizer (ca. 5 phr) to prevent the compound from suddenly darkening during fusion as a result of the inclusion of zinc in the stabilizer system.

Barium: Holds color for long-term heat exposure.

Cadmium: Good color during early fusion stages.

Zinc: Similar to cadmium but will darken compound quickly unless balanced with epoxy; used to minimize sulfur staining.

Lead: Excellent for long term heat stability; has pigmenting effect; excellent activator for foams based on Celogen® AZ.

Volatile diluents.

In the preparation of organosols based on Marvinol 50, it is not necessary to use the highly polar ketones

© U.S. Rubber registered tradename for its blowing agents.

and aromatics as was the case with the early copolymer organosol resins. Aliphatic naphthas, such as VM&P and mineral spirits, etc., are recommended along with those aliphatic diluents whose aromatic components have been removed. The latter materials made primarily for the odorless paint field, although slightly more expensive are excellent for maintaining good viscosity stability.

The boiling range of the diluent selected will be dependent upon the plastisol's processing conditions. In the case where there is considerable exposure of the unfused organosol prior to coating or where there is the danger of rapid fusion trapping diluent in the film, a slow evaporating or high boiling diluent is desirable. On the other hand, too high a boiling range may result in some diluent remaining in the film after fusion.

Another consideration in diluent selection is the compatibility of the diluent with the plasticizer system. Many polymeric type plasticizers are not compatible with aliphatic hydrocarbons and, in such an instance, diluent blends high in aromatic content are required.

Fillers.

Mineral fillers are many times added to reduce per pound costs. It should be recognized, however, that the pound-volume cost is not reduced as dramatically as the pound cost due to the higher density of the filler

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in comparison with the plastisol: for example, 2.6 for calcium carbonate versus 1.2 for a typical plastisol compound.

Although fillers are selected primarily on the basis of cost, a few additional considerations are of importance. Their effect on viscosity may be minimized by the selection of a low oil absorption type. They must not be excessively coarse so as to cause any wear on processing equipment such as mixers and paint mills. Such wear on equipment will also result in a graying of the plastisol due to the presence of the particles of eroded metal.

Fillers used in plastisol work are generally of the calcium carbonate type which are available at low cost in a variety of particle sizes and surface treatments.

Pigments.

The selection of pigments must be made on the basis of their ability to withstand color changes during the fusion cycle and the exposure to which the plastisol will be subjected in use. Such information is available in considerable detail from pigment manufacturers.

Of practical importance to many plastisol users who are not in a position to prepare their own pigment dispersion is the availability from several suppliers of pigments dispersed in plasticizer, made especially for the plastisol field.

Miscellaneous ingredients.

Through the use of various formulating ingredients

in addition to those just discussed the plastisol compounder is capable of applying considerable finesse to his work.

Some of these materials are high oil absorption pigments, surfactants, thermosetting plasticizers and toners. The functions of these miscellaneous ingredients are described below.

High oil absorption pigments are used in small quantities to build yield value in plastisols for cold dip type applications and to prevent cloth penetration in glove dipping and spread coating.

Another approach to the development of yield value in plastisols is through resin selection. Here Marvinol X 6215S and blends with Marvinol 50 may be utilized to build yield value.

Surfactants are used as viscosity depressants. A typical surfactant is Polyethylene glycol 400 dioleate.

Thermosetting plasticizers are used to produce rigid plastisols without resorting to the use of volatile diluents. They also impart good heat distortion properties. These systems are generally handicapped by high cost and poor heat and viscosity stability.

Toners are violet dyes or fluorescent agents that help offset the yellowish cast developed in many clear plastisols on fusion. This is of particular value in the clear plastisol boot field. A typical toner is Alizarine Irisol "N" (General Aniline & Film Corp. Dyestuff & Chemical Division).



Marvinol 50 is readily compounded with standard mixing equipment, techniques.

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

For the bulk of plastisol and organosol compounding, the change can or pony type mixer pictured here is quite adequate.

A normal mixing cycle would involve charging the mixer with sufficient plasticizer, or plasticizer and diluent in the case of an organosol, to wet the resin into a fairly heavy paste. This allows for the effective transmission of shear forces throughout the mix. When all the resin has been thoroughly wetted and dispersed, 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 low speed, high-shear mixing technique may be satisfactorily applied to virtually all 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 mixer which does away with the necessity of keeping the paste in a heavy stage for effective mixing. Known as a "high-speed, high-shear" mixer, it is best

used for low viscosity plastisols and organosols.

Since 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 would be first blended in the mixer after which the resin is added in increments.

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

Occasionally, inadequate mixing or improper mixing procedures will allow for undispersed resin agglomerates working their way into the finished compound. In such instances a single, loose pass through a three-roll paint mill is sufficient to disperse any such resin clusters.

When deaeration is necessary, a variety of vacuum set-ups will accomplish this.

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There are seven other Marvinol plastisol resins and three different blending resins.

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In addition to Marvinol 50, U.S. Rubber can supply any of the following plastisol resins with more to come in the future, all meeting industry's sophisticated demands for specialty dispersion resins.

Dispersion resins	Marvinol 51	Readily stirred into plasticizers to form plastisols with low Brookfield viscosity and outstanding air release properties. Excellent for slush molding, rotational casting, chemically blown plastisol foam.
	Marvinol 53	Readily stirred into plasticizers to form plastisols of outstanding quality with respect to chemically blown foam. Also, well-suited to processing conditions requiring reduced gelation time, low viscosity and excellent air release, e.g. slush molding, rotational casting, hot and cold dipping, etc.
	Marvinol 55 (X-6116)	A stir-in copolymer dispersion resin designed for lower fusion temperature applications. High viscosity and rapid gelation features control cloth penetration.
	Marvinol 56	A stir-in copolymer plastisol resin combining low Brookfield and Severs viscosity properties with rapid gelation and low fusion temperature properties. Ideally suited for a wide variety of plastisol casting, molding, and adhesive applications, where a combination of low temperature fusion and low application viscosity is required for more rapid processing or in the coating of heat sensitive substrates.
	Marvinol X-6085	A stir-in homopolymer with uniquely low viscosity properties. Also provides excellent gloss control.
	Marvinol X-6215S	A plastisol resin that's well-adapted to high plasticizer level compounds where high viscosity and yield are required to develop strike-through resistance. Excellent for chemically blown foam.
	Marvinol X-6501	A stir-in copolymer dispersion with uniquely low-viscosity properties combined with low-fusion temperatures.
Blending resins	Marvinol 10	High molecular weight resin. Reduces viscosity, enhances air release in plastisol formulations.
	Marvinol 24PL	A low cost blending resin for plastisol compounds. Reduces viscosity and enhances air release. Excellent for chemically blown foam compounds.
	Marvinol 15	A low cost blending resin for plastisol compounds where paint mill processability is desired. Reduces viscosity and enhances air release. Excellent for chemically blown foam compounds.

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Recipes to use as a guide.

When discussing plastisol and organosol formulations, it is only possible to present them in a most general manner. The actual production recipe will, in many cases, bear only a slight resemblance to the "starting point" recipe. As a guide, however, the following recipes are presented. Perhaps their greatest value will be to illustrate the principles behind the use of the various ingredients. Further details on these formulations for other applications are available through our technical sales representatives.

The use of Marvinol resins other than 50 has been indicated where such resins were specifically designed for that particular application.

A. Paper and fabric coating.

This is a basic recipe for high gloss and general purpose coating onto paper, fabric and other substrates. The use of diluent for high-shear viscosity adjustment will depend upon coating speed and thickness, plasticizer level and type, etc. Generally an intermediate low-shear (Brookfield) viscosity provides an optimum for vacuum deaeration, pigment floatation resistance and fabric penetration control. A balanced stabilizer system including epoxy plasticizer is used.

B. Low cost, low gloss coating.

For paper and fabric coating, the use of a controlled particle size blending resin and filler lower compound gloss as well as cost with only a minimal loss in physical properties.

C. Organosols.

The use of aliphatic diluent and surface active agent

enables the formulation of low-stable viscosities at low plasticizer levels. Here again the high gloss characteristics of Marvinol 50 make it an exceptional resin for flooring and paper coating.

D. Slush and rotational molding.

Marvinol 51 and 10 combine to provide exceptionally low viscosity, excellent air release, high hot strength and high physical properties at room temperature. Marvinol 10 provides a roughened air surface which is essential in footwear.

E. Foam.

High temperature blowing agents (Celogen AZ) are most popularly used in vinyl foam. Here Marvinol 53 used alone or combined with a high viscosity resin, Marvinol X6215S for cloth penetration control provides an optimum in foam quality and physical properties.

F. Semi-rigid plastisol.

A unique resin, Marvinol X6085 combined with Marvinol 24PL provides exceptionally low viscosity. This enables a marked reduction in plasticizer level.

G and H. Low fusion temperature.

A copolymer dispersion resin, Marvinol 56 combined with a high solvating plasticizer provides exceptionally low fusion temperatures. Through the use of Marvinol X6501, low fusion is combined with low gloss and ultra-low viscosity.

I. Food closure and non-fog.

Marvinol 50 and X6085 have unusually good taste and odor integrity for a variety of food closure

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applications. These resins are equally useful in non-fog automotive applications. These qualities result from the low level and careful selection of the non-PVC ingredients used in these resins. Marvinol 50 may be combined with Marvinol 10 in these applications for a further enhancement of properties plus improvements in air release, viscosity and cost. Of course plasticizer and stabilizer selection are equally important.

APPLICATION →	A	B	C	D	E	F	G	H
	Paper and fabric coating.	Low gloss, low cost coating.	Organosol.	Slush and rotational molding.	Foam.	Semi-rigid plastisol.	Low fusion.	Low fusion, low gloss, low viscosity.
Marvinol 50	100	70	100	—	—	—	—	—
Marvinol 51	—	—	—	70	—	—	—	—
Marvinol 53	—	—	—	—	70	—	—	—
Marvinol 56	—	—	—	—	—	—	100	—
Marvinol X6085	—	—	—	—	—	60	—	—
Marvinol X6215S	—	—	—	—	30	—	—	—
Marvinol X6501	—	—	—	—	—	—	—	100
Marvinol 10	—	—	—	30	—	—	—	—
Marvinol 15	—	30	—	—	—	—	—	—
Marvinol 24PL	—	—	—	—	—	40	—	—
TCP	—	—	—	—	—	—	60	60
DOP	60	60	30	35	95	—	—	—
DCP	—	—	—	35	—	35	—	—
Extender plasticizer	—	—	—	—	—	—	10	10
Epoxy plasticizer	5	5	5	5	5	5	5	5
Aliphatic diluent	2	—	10	—	—	—	—	—
Dibasic lead phthalate ⁽¹⁾	—	—	—	—	3	—	—	—
Ba, Cd, Zn stabilizer	3	3	3	3	—	3	3	3
PEG 400 dioleate	—	—	1	—	—	—	—	—
Celogen AZ	—	—	—	—	3	—	—	—
Ca CO ₃ filler	—	20	—	—	—	—	—	—
Pigmentation	5	5	—	—	—	—	—	—

(1) Dythal-National Lead Company



Where to get
more information.

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If you'd like more information about our products please call or write the district sales office most convenient to you. Or if you prefer, write directly to our division headquarters.

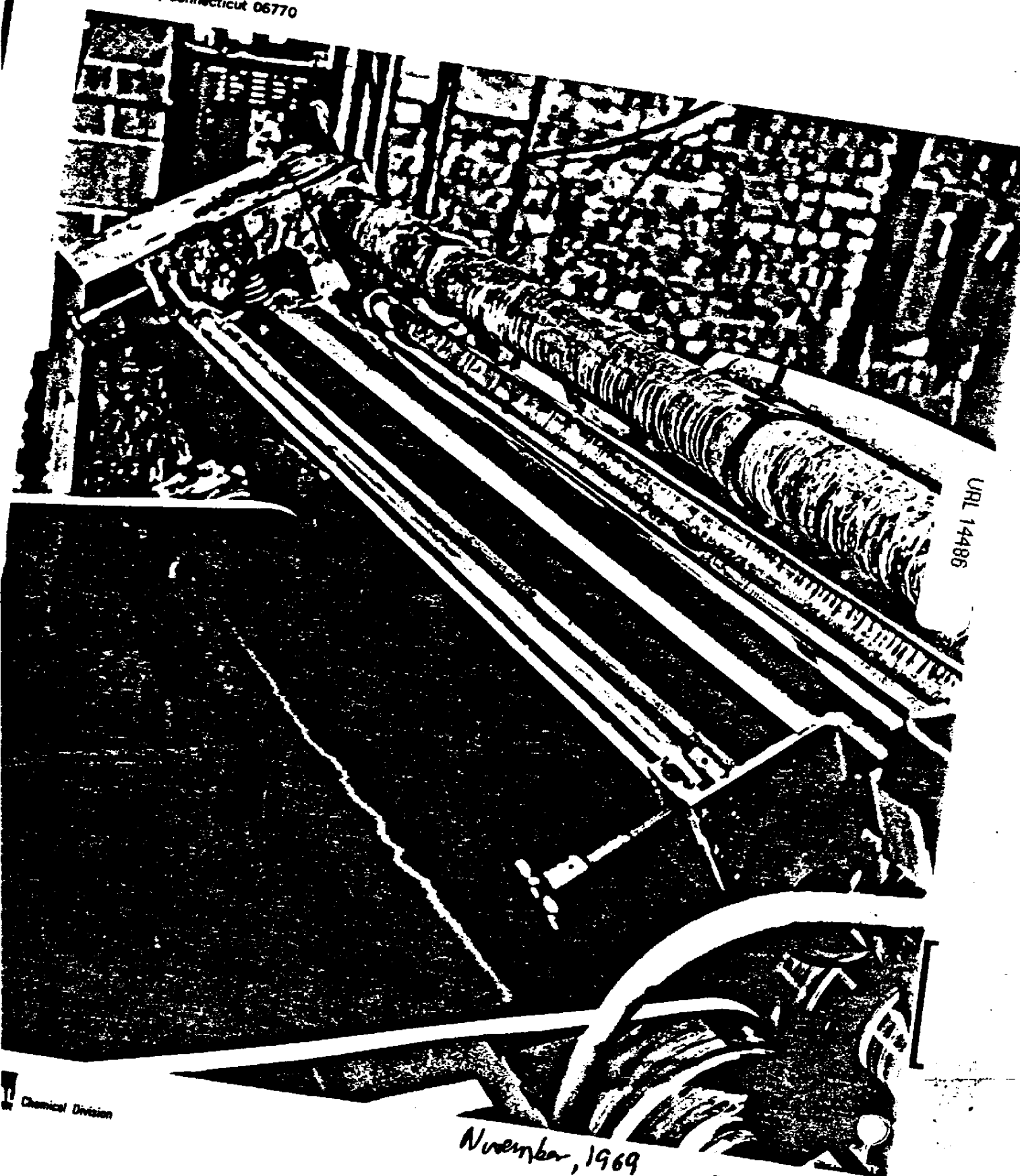
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Dallas	U.S. Rubber Company, Chemical Division, 1011 Regal Row, Dallas, Texas 75247	214-631-2310
Dalton	U.S. Rubber Company, Chemical Division, P. O. Box 371, Dalton, Georgia 30720	404-278-1911
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Los Angeles	U.S. Rubber Company, Chemical Division, 5901 Telegraph Road, Los Angeles, California 90022	213-723-9971

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	Cable address: UNIROYAL, New York	

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