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Solventless Processing of Modified Poly(vinyl Fluoride) and its Properties*

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Synopsis

The properties of fluorocarbon plastics have made them very desirable for numerous new applications. The DALVOR X-6500 series of fluoropolymers can be easily fabricated without the use of solvents. General compound information, including pigmentation, lubrication, and rheology data, is presented as well as chemical resistance, weathering, and electrical data. Processing parameters for producing both flat and blown films are given, along with recommended types of equipment. Data are presented on fluid bed coating and various other applications are discussed.

INTRODUCTION

Historically, the use of poly(vinyl fluoride) (PVF) has been limited to solvent-extruded free film or as a dispersion resin for bake-on coatings on metal substrates. Because of the narrow temperature range between the melting point and decomposition point of PVF, it has been necessary to use high boiling solvents as processing aids for film extrusion.

The present series of DALVOR X-6500 resins represent a modified PVF which is melt processable without the use of solvents. The DALVOR X-6500 series of fluoropolymers are free-flowing powders which provide a combination of excellent weathering, stain resistance, and electrical properties with ease of fabrication. Products of the Diamond Shamrock Corporation, these fluoropolymers are available commercially and are closely related to DALVOR 720 poly(vinyl fluoride) previously reported.[1,2]

The purpose of this paper is to summarize the important end use and processing properties of the DALVOR X-6500 series of resins and describe in greater detail the development of typical applications. Some applications and associated processes to be discussed are currently under development and are subject to improvement as more information becomes available. The present series of resins consist of X-6501, X-6502, and X-6503.

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END USE PROPERTIES

The modified PVF resins show the general characteristics of fluoropolymers, i.e., excellent ultraviolet resistance, chemical inertness, and low temperature flexibility. These properties coupled with low solubilities, low coefficient of friction, and low refractive index have been utilized in the development of end use properties.

TRANSPARENCY

Films made from natural grades of the DALVOR X-6500 series have visible light transmission of 80%–90% (ASTM D-1746), which is about 10%–20% higher than presently available poly(vinyl fluoride) polymers. In film thicknesses up to about $^1/_{16}$ in., the resins have water-white clarity. The polymer is also fairly transparent to ultraviolet radiation and possesses excellent weathering properties as will be shown below.

WEATHERING

Both clear and pigmented films of the DALVOR X-6500 series show excellent weatherability. For example, films exposed 7000 hr in the Xenon Arc Weather-Ometer showed no significant change in tensile strength, color, or gloss. Similarly, films exposed two years in Florida have not changed significantly in these properties. Figure 1 shows chalk rating

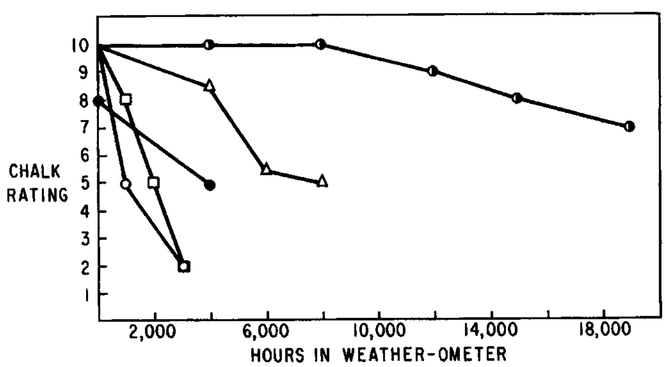

Fig. 1. Chalk rating of white-pigmented films vs. Weather-Ometer exposure: (○) melamine alkyd film; (□) acrylic film; (●) commercial PVF film; (△) commercial PVF_2 film; (◑) DALVOR X-6501 film.

versus hours of exposure in the Weather-Ometer for X-6501 and competitive films. Good resin-pigment wetting is believed to be the cause for the high chalk rating versus time.

Another application of excellent weathering performance is synthetic turf. A 2 × 50 mil green monofilament of X-6501 was extruded and exposed in the Xenon Arc Weather-Ometer for 10,000 hr. The mechanical properties of the exposed and unexposed fibers are shown in Table I.

TABLE I
Weatherability of Synthetic Turf Green-Pigmented DALVOR X-6501
0.05 × 0.002 Inch Monofilament

Exposure in Xenon Arc Weather-Ometer, hr	Tensile strength, psi	Elongation, %
0	30,000	80
10,000	24,000	50

SPECIFIC GRAVITY

The specific gravity of the DALVOR X-6500 resins is 1.34 to 1.36, the lowest of all commercially available fluoropolymers. Aside from the fact that light-weight articles can be fabricated from these resins, their low specific gravity implies a significant volume cost advantage. For example, at equivalent cost per pound, the DALVOR X-6500 resins would have 31% greater film coverage than commercial poly(vinylidene fluoride). In spite of the low specific gravity, films from the DALVOR X-6500 series have a relatively low gas permeability—roughly equivalent to that of poly(ethylene terephthalate). These properties are shown in Table II.

TABLE II
Relative Permeability[c] of Polymeric Films
to Nitrogen, Oxygen, and Carbon Dioxide[a]

Polymer	N_2		O_2		CO_2	
	°C	$P \times 10^{10c}$	°C	$P \times 10^{10c}$	°C	$P \times 10^{10c}$
Poly(vinylidene chloride) (Saran)	30	0.00094	30	0.0053	30	0.03
Cellulose (Cellophane)	25	0.0032	25	0.0021	25	0.0047
Poly(6-aminocaproic acid) (Nylon 6)	30	0.0095	30	0.038	30	0.088
Poly(ethylene terephthalate) (Mylar)[b]	30	0.011	30	0.045	30	0.15
DALVOR X-6501 (1.0 mil)	25	0.017	25	0.064	25	0.375
					35	1.08
Poly(vinyl chloride)	30	0.11	30	0.30	30	1.50
Rubber hydrochloride	30	0.14[d]	30	0.54[d]	30	1.30[d]
Polyethylene, high-density	30	0.18	30	0.51	30	2.10
Polystyrene	30	0.29	30	1.10	30	8.80
Polycarbonate	25	0.30	25	1.40	25	8.00
Polypropylene	30	0.44	30	2.30	30	9.20
Polyisoprene (natural rubber)	25	8.20	25	23.80	25	135

[a] Data source: Brandrup and Immergut.[3]
[b] Du Pont's registered trademark for polyester film.
[c] P in units of $(cm^3)\ cm/(sec)(cm^2)(cm\ Hg)$.
[d] Plasticized film.

CHEMICAL AND STAIN RESISTANCE

The DALVOR X-6500 resins have high resistance to alkalies and most inorganic acids which are not highly oxidizing in nature. For example, 1-mil clear films of DALVOR X-6503 were exposed to variety of chemicals at 50°C. After two and four weeks of exposure there was little effect on film properties. These data are seen in Table III.

Both clear and white films of DALVOR X-6501 were subjected to the following staining agents at room temperature for 24 hr: orange juice, grape juice, tea, coffee, mustard, vegetable oil, catsup, crayon, lipstick, blood, and shoe polish. The films were then washed with mild detergent. In each case, the stain was completely removed from the film.

TABLE III
Chemical Resistance Tests on DALVOR X-6503 Clear 1-Mil Film[a]

	Weeks exposure					
	0		2		4	
Chemical	Elongation, %	Tensile strength, psi	Elongation, %	Tensile strength, psi	Elongation, %	Tensile strength, psi
Glacial acetic acid	140	3900	140	2600	135	4300
n-Butanol	140	3900	140	5500	130	4600
n-Heptane	140	3900	130	3600	130	6300
Perchloroethylene	140	3900	130	6280	125	5600
35% HF	140	3900	140	5200	140	5500
50% NaOH	140	3900	135	3300	100	2800

[a] Conditions: Immersion 0 to 4 weeks at 122° F.

MECHANICAL PROPERTIES

Table IV shows that the physical properties of DALVOR are comparable to those of other fluoropolymers. These values are equal or superior to those for most other fluorine-containing polymers (PTFE, PCTFE, PVF_2, and FEP). PVF (Tedlar) offers high mechanical properties, but the data in the table are given only on solvent-extruded oriented film. The base resin is not available commercially.

ELECTRICAL PROPERTIES

The electrical properties of DALVOR X-6501 compare quite favorably with those of the other fluoropolymers shown (see Table IV). These properties, coupled with ease of fabrication, make the DALVOR resins ideal for electrical applications, particularly where humidity and ultraviolet radiation are high.

DAVOR X-6500 films also exhibit superior abrasion resistance compared to other films. The results of the falling sand abrasion test are shown in Table V. The abrasion coefficient is the liters of sand required to just erode the film to bare metal.

TABLE IV
Properties of DALVOR Resin and Other Fluorine-Containing Resins[a]

Property	ASTM Test	PTFE	PCTFE	PVF[b]	PVF_2	FEP	DALVOR
Specific gravity	D-792	2.1–2.3	2.1	1.38–1.40	1.76	2.16	1.34–1.36
Tensile strength, psi	D-638	2500–3800	4300–5700	9600–19,000[c]	4500–6000	2700–3100	4200–5200
Elongation at break, %	D-638	200–300	100–200	110–260	100–300	250–350	160–350
Izod impact, ft-lb/in.	D-256	2.0	1.2–1.3	—	3.5	2.9	3.0
Water absorption, %	D-570	0.005	nil	<0.5	0.04	nil	0.05–0.12
Dielectric strength, volts/mil (1 mil at 60 cps)	D-149-64	4300	1000–3700	3500	—	5000	3110
Dielectric constant at 1 kc	D-150-64	2.1	2.6	8.5	7.72	2.0	2.09
Dissipation factor at 1 kc	D-150-64	0.0002	0.023	0.02	0.019	0.0002	0.014
Volume resistivity, ohm/cm	D-257-61	10^{18}	10^{18}	10^{13}	10^{14}	10^{19}	10^{14}

[a] PTFE, polytetrafluoroethylene; PCTFE, polychlorotrifluoroethylene; PVF, poly(vinyl fluoride); PVF_2, poly(vinylidene fluoride); FEP, a copolymer of hexafluoropropylene and tetrafluoroethylene; DALVOR, a modified PVF.

[b] Tests on Tedlar Film (oriented), du Pont registered trademark.

[c] Different test method.

TABLE V
Abrasion Resistance of White Plastic Films[a]

Type of coating	Abrasion coefficient, l./mil
DALVOR X-6501	58
Commercial PVF	46
Polypropylene	40
Polytetrafluoroethylene	34
Epoxy	28
Acrylic	26
Epoxy phenolic	22
Silicone polyester	14
Alkyd	12
Polyester	11

[a] ASTM Test D-968-51.

The particle size distribution of DALVOR X-6502 resin is shown in Figure 2. The resin particles are large enough to flow easily in an extruder hopper. They also fluidize easily for fluidized bed coating applications.

Table VI shows a typical stabilizer system for these resins. In establishing processing conditions, it is important to recognize that DALVOR X-6500 resins have a relatively broad melting range with relatively low

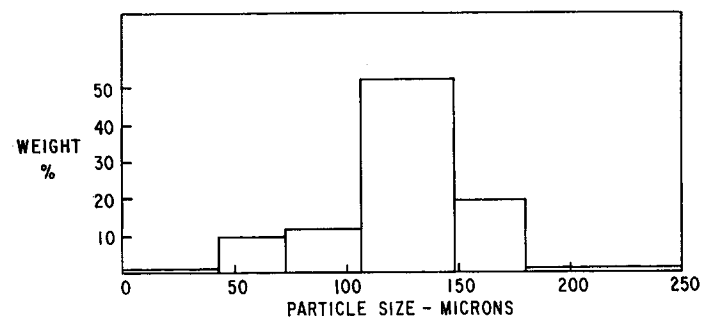

Fig. 2. Particle size distribution: X-6502 resin.

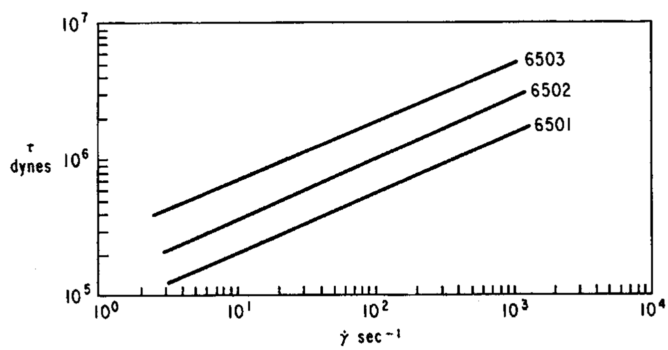

Fig. 3. Shear stress (τ) vs. shear rate (γ) at 375° F.

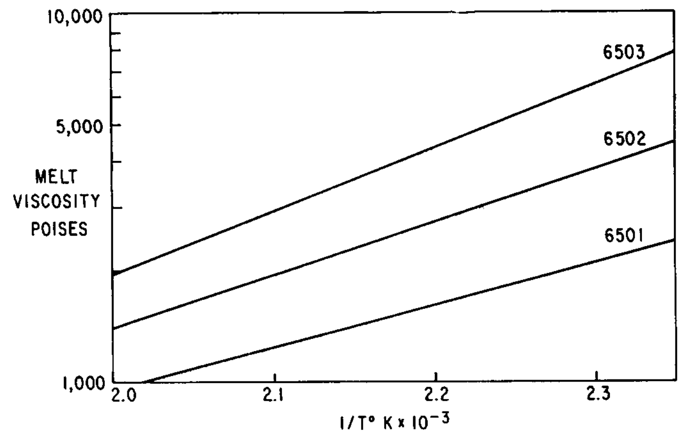

Fig. 4. Melt viscosity vs. temperature at 10^3 sec^{-1} shear rate.

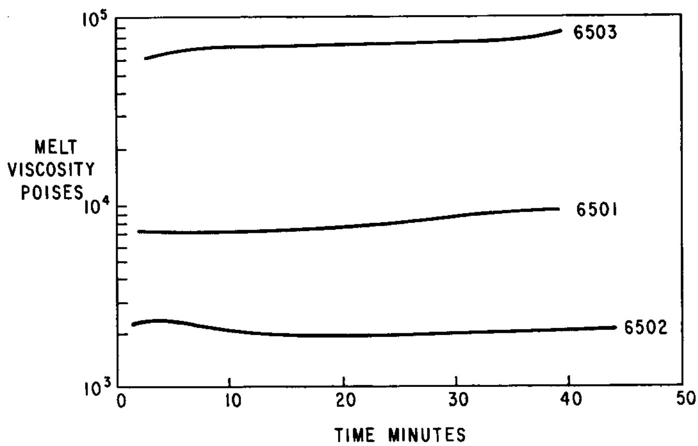

Fig. 5. Shear stability of stabilized resins at 420°F at 10 sec^{-1} shear rate.

melt viscosities. The use of a lubricant helps prevent stagnant flow in recessed areas of the processing equipment.

Typical rheology plots are seen in Figure 3. They were run on the Sieglaff-McKelvey rheometer at 375°F. The resins were run at several temperatures and a melt viscosity versus temperature graph constructed for high shear (10^3 sec^{-1}), as shown in Figure 4.

The shear stability of the stabilized unpigmented resins is shown in Figure 5. This test was more valid than oven tests which did not correlate well with extrusion conditions. Unstabilized resins show poor shear stability in a relatively short period of time.

DALVOR resins, like PVC resins, can undergo degradation with heat and time. The decomposition to hydrogen fluoride is somewhat faster than that of PVC to hydrogen chloride.

DALVOR resins can be pigmented, but care should be taken in pigment choice, since some trace oxides such as SiO_2 and Al_2O_3 present in pigments can cause a decrease in stability.

Further tests were conducted in a Brabender extruder, shown in Table VII. The use of lubricants significantly decreased torque and improved rate and surface appearance.

These data were used for scale up to a $2^1/_2$-in. extruder shown in Table VIII.

TABLE VI
Stabilization of DALVOR X-6500 Resins

Compound	Recommended level, phr[a]
Tridecyl phosphite	0.25–0.75
Dipentaerythritol	0.25–0.75
2,6-Di-*tert*-butyl-*p*-cresol	0.25–0.75
Wax OP	0.05

[a] Parts per hundred parts resin.

TABLE VII
$^3/_4$-Inch Extrusion Data[a]

	Parts by weight				
DALVOR X-6502	100	100	100	100	100
Stabilizer	3	3	3	3	3
Ester Wax A		0.5			
PE Wax			0.25		
Ca stearate				0.5	
Ester Wax B					0.5
RPM	50	50	50	50	50
Pressure die, psi	2150	2250	2900	1800	2750
Torque, M-g	3700	1600	1700	2250	1900
Rate, g/min	33	37.5	36	36.8	36.4
Stock temp., °F	345	320	325	325	330
Surface	fair	excellent	excellent	excellent[b]	excellent

[a] A $^1/_4$-in.-diameter die was used for testing with an extruder profile of 330°F, 330°F, and 350°F.

[b] Very cloudy and unmelted lubricant could be seen in the rod.

TABLE VIII
Extrusion Conditions for DALVOR X-6500 Resins

	Feed	Metering	Die	Die lips
Temperature, °F				
X-6501	250	330	350	400
X-6503	250	350	370	420
$2^1/_2$ in. Screw, Flight depth, in.	0.420	0.150	—	—
L/D 20:1–24:1				
Compression ratio 2.2:1–3.0:1				

It is recommended that for optimum surface gloss and clarity, high temperatures (425°–470°F) be used at the die lips to polish the extrudate.

Dies used for DALVOR resins should be streamlined to allow smooth flow without any points of hangup. These polymers have acceptable stabilities at processing temperatures, but any point of poor flow can present problems during long runs. This streamlining has been found to be very important in blown film systems. Long adapter sections from the extruder to the dies can present serious problems. Choker bars for flat dies are also not recommended.

DALVOR resins have also been fluidized and coated onto preheated metal parts. A temperature of about 600°F was needed to completely fuse out a film. Films put on this way show good clarity and chemical resistance. Table IX shows the chemical resistance of rods preheated to 625°F and coated with DALVOR X-6502.

TABLE IX
Chemical Resistance of DALVOR X-6502
Fluidized Bed Coating (8 mils) Over Steel[a]

Chemical	Days	Results
H_2SO_4, 50%	60	one small blister[b]
Acetic acid, 10%	8	small blisters
Xylene	60	no change
NaOH, 20%	60	no change
Trisodium phosphate, 5%	60	no change
Zinc chloride, saturated	60	no change
Ethanol	60	no change
Butyl acetate	60	no change
Phosphoric acid, 85%	60	no change
Caprylic acid	41	no change

[a] 50% Immersion at 150°F.
[b] Blister appeared to be caused by a pinhole.

APPLICATIONS

Having discussed the key properties and processing characteristics of the DALVOR X-6500 resins, let us consider their applications. These polymers, because of their excellent properties and ease of processing, should open many new applications. Some of the more normal applications are discussed below.

The weathering properties of DALVOR resins make them useful as laminated films or hot-melt coatings. Both clear and pigmented films have been laminated to steel, aluminum, and plywood substrates. Clear films with ultraviolet screeners can also provide a decorative surface and impart weathering resistance to polymeric substrates such as polyesters, ABS, polystyrene, poly(vinyl chloride), etc. The ultraviolet transmission suggests that these resins can be used in greenhouses, solar distillation units, and plant covers. DALVOR films can be laminated to substrates for applications where stain resistance is required. Typical uses are for wall coverings for hospitals, bathrooms, kitchens, and airplane cabins where hard-to-remove stains are a problem. Excellent stain resistance has been demonstrated with both clear and pigmented films.

Because of their good electrical insulating properties, DALVOR resins can be used as the primary insulation for wires where thin coverings are required, such as for computer circuitry. These resins show excellent resistance to cut-through and are yet flexible enough to allow connections without undue spring-back.

The use of DALVOR resins as fluid bed coatings opens other possible uses where protective coatings are needed on irregularly shaped parts. Thin coatings (less than 8 mils) are, however, difficult to achieve on some irregularly shaped parts and areas of high heat retention will fuse out in thicker films.

CONCLUSIONS

DALVOR X-6500 resins exhibit excellent physical and electrical properties with superior weathering resistance. They also can be processed without a solvent at fairly low temperatures using conventional equipment. These resins can be easily stabilized, lubricated, and pigmented. Characteristics such as these in a fluorine-based polymer are unique and allow a wide variety of applications.

We are indebted to Dr. C. L. Sieglaff, who furnished the rheological data.

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