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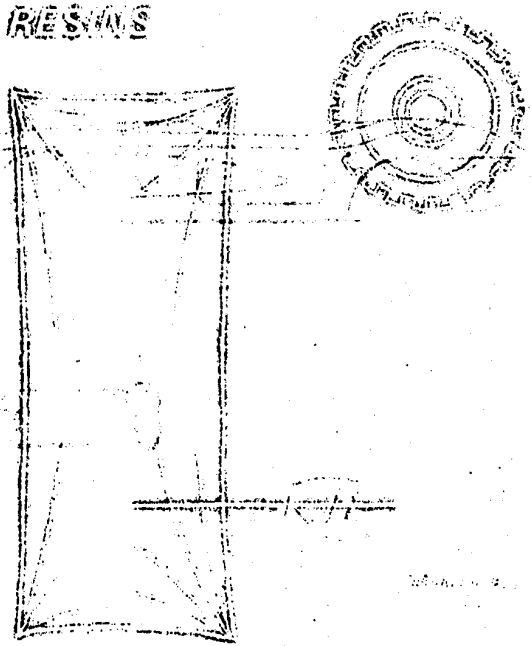
Monsanto

PLASTICIZERS FOR HARD TO PLASTICIZE RESINS



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Furthermore, nothing contained herein shall be construed as a recommendation to use any product in conflict with existing patents covering any material or its use.

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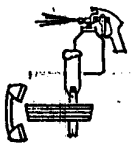

INTRODUCTION

Hundreds of plasticizers are commercially available to plasticize and modify vinyl, cellulosic, and other easily-plasticized resins. Yet there are numerous unfilled needs for suitable plasticizers for many other resins, especially some of the thermosetting resins, that are more difficult to plasticize satisfactorily. Many formulators require just the right plasticizer to improve the performance of a particular resin in an existing application, to make it suitable for a new application, or to improve its economics to expand its market.

Often the best solution to these difficult and demanding plasticizing problems already exists among Monsanto's more-than-eighty plasticizers. Monsanto's Plasticizer Council, with its years of cumulative experience with virtually every kind of commercial resin, offers unmatched competence and know-how with which to seek and find answers to the toughest plasticizing requirements.

This bulletin has been prepared to give you some idea of the breadth and versatility of Monsanto's knowledge, experience, and plasticizers. We hope that you will consult it often for preliminary information about resins that require a plasticizer or that could be improved by the use of a better plasticizer.

For more detailed information, we will gladly send you Monsanto technical bulletins on indicated plasticizers or on the general application area. Of course your specific inquiry to the Plasticizer Council, directed either to the nearest Monsanto District Sales Office or to the Plasticizer Sales Department in St. Louis, will receive prompt, expert attention.

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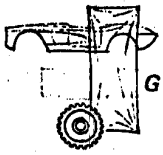

GUIDE TO MONSANTO PLASTICIZERS FOR HARD-TO-PLASTICIZE RESINS

Plasticizer	Acrylic	Epoxy	Polyester	Polyamide		Phenolic	Melamine	Chlorinated rubber	Styrene-Butadiene	Neoprene
				nylon	dimer acid-based					
Phthalates										
dibutyl	X	X	X			X		X	X	
dicyclohexyl	X									
diethyl	X									
diisodecyl	X									
dimethyl	X		X							
dioctyl	X								X	
diphenyl										
SANTICIZER® 160	X		X			X			X	
SANTICIZER 165	X									
SANTICIZER 213										
Adipates										
diisodecyl										
dioctyl										
Phosphates										
Tricresyl	X	X	X			X	X	X	X	
Triphenyl								X		
SANTICIZER 140	X	X					X			
SANTICIZER 141	X	X								
Glycolates										
SANTICIZER E-15		X								
SANTICIZER B-16	X	X						X	X	
SANTICIZER M-17		X								
Sulfonamides										
SANTICIZER 1-H				X	X					
SANTICIZER 3				X	X					
SANTICIZER 8		X		X	X	X				
SANTICIZER 9			X	X	X	X	X			
SANTOLITE® MHP				X	X		X	X		
SANTOLITE MS-80%				X	X					
Other										
HB-40®						X				
MOD-EPOX®		X								
Triphenyl Phosphite			X							
MONTAR®										
AROCLOR®		1221 1254 1248 1260 5460 1262	1260 4465 5460		X	1268 5460 2565 1262		X	X	1268 5460
SANTICIZER 409	X									
SANTICIZER 411										

®SANTICIZER, SANTOLITE, HB-40, MOD-EPOX, MONTAR, and AROCLOR are Monsanto Chemical Company trademarks, registered in the U. S. Patent Office.

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X-marks denote the plasticizers mentioned in this bulletin as being most generally useful in the indicated resin. Since other plasticizers may be used for special applications, and since Monsanto is constantly adding to its vast fund of knowledge about plasticizer/resin systems, it is always a good idea to ask Monsanto's Plasticizer Council for advice on difficult or unusual plasticizer-formulation problems.

Polybutene	Nitrile rubber	Polysulfide	Silicone rubber	Crepe rubber	Polyvinylidene chloride	Vinylpyrrolidone Homopolymer	Vinylpyrrolidone Vinyl Acetate Copolymer	Casein	Zein	Soya	Allyl starch	Shellac	Asphalt
	X	X			X		X	X	X	X	X		
					X								
	X												
						X	X						
	X				X								
					X								
	X				X			X	X	X	X		
							X						
	X												
	X												
	X												
					X			X	X	X	X		
	X							X	X	X	X		
	X				X	X	X						
					X	X	X						
	X				X		X	X	X	X	X	X	
					X								
								X	X				
		X						X	X			X	
					X				X			X	
						X	X		X				
								X	X				
	X	X											X
		X											
X		1222	X	1262	8468			X	X	X	X		8468
	X												
	X												

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ACRYLIC RESINS

Polymers of acrylic and methacrylic acids and esters are noted for their clarity and outstanding light and weather resistance. They are widely used in extrusions, sheet, injection moldings, castings, fibers, and adhesives.

A major expanding use of acrylic resins is in solution coatings, where they impart exceptional durability, light-fastness, hardness, and high gloss upon polishing. Since acrylic and acrylic-modified lacquers have performed so exceptionally under the tough conditions imposed by automobiles and aircraft, they are becoming increasingly accepted in both air-dry and baking lacquers for other metal-finishing applications, including appliances, machinery, motors, furniture, and shipping drums.

Poor adhesivity of acrylics to the substrate is a major deficiency that can be overcome only by the use of external plasticizers. Suitable plasticizers, therefore, must impart adhesion and should also improve flexibility, durability, and gloss; reduce sensivity to moisture and high humidity; improve economics by extending the more costly resin; and have the least effect on the desirable properties of the acrylic resin.

SANTICIZER 160 has become the standard plasticizer for polymethyl methacrylate because it offers the best balance of desirable properties and has the best cost/performance characteristics. Acrylic coatings plasticized with SANTICIZER 160 offer excellent adhesion, gloss, humidity compatibility, levelling, flexibility, light stability, and cold-check resistance.

Dicyclohexyl phthalate is sometimes used with SANTICIZER 160 to achieve harder lacquers and to improve moisture resistance. SANTICIZER 409, a polymeric plasticizer, is incompatible with acrylic resins, but when used with SANTICIZER 160 it reduces the plasticizer loss by volatilization.

In Monsanto's continuing research and development programs to produce ever-better plasticizers, several promising candidates are equal to or better than SANTICIZER 160 in most important qualities yet are much less volatile.

Performance characteristics of various plasticizers with acrylic resins are compared with those of SANTICIZER 160 as the standard plasticizer in Table I. (Plus signs indicate that the plastizer performs better than SANTICIZER 160 in the indicated property; minus signs denote poorer performance.)

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TABLE I—PLASTICIZER PERFORMANCE IN ACRYLIC RESIN

Plasticizer	Solvency[a]	Volatility[b] (100°C, 23 hr.) Plast. Lost (%)	Repairability[c] (Solvent Craze)	Humidity[d] Stability	Light[e] Stability (gloss)
NONE			— —	equivalent	84
SANTICIZER 160	Standard	44.0 (Std)	Standard	Standard	78 (Std)
Dimthyl Phthalate	+	43.8			
Diethyl Phthalate	++	41.7			
Dibutyl Phthalate	equivalent	46.3	+		
Dioctyl Phthalate	— —	41.5	— —	—	
Diisodecyl Phthalate	— —	4.5			
SANTICIZER 165			—	—	
SANTICIZER B-16	equivalent	49.7		— —	67
Dicyclohexyl Phthalate	—	29.0		—	
DCHP/SANTICIZER 160 (2/1)	—	30.0			80
DCHP/SANTICIZER 160 (1/2)			equivalent		
Tricresyl Phosphate	—	12.4	++	—	80
SANTICIZER 140	—	31.0		— —	67
SANTICIZER 141	equivalent	45.2		—	75
SANTICIZER 409	Incompatible — cloudy film				
SANTICIZER 409/SANTICIZER 160 (2/1)	— —	27.5	slight neg.	equivalent	
SANTICIZER 409/SANTICIZER 160 (1/1)					71
SANTICIZER 409/SANTICIZER 160 (1/2)	— —	36.3	slight neg.	equivalent	

a) Solvency compared to that of SANTICIZER 160 in one or more of three ways: film solvation, gel temperature of plasticizer-resin mixture or of plasticized-lacquer system, and viscosity of plasticized lacquers.

b) Values for volatility may also include solvent loss because of poor solvent release.

c) Comparison of observed checking after either 3-minute immersion of plasticized-lacquer on tinplate into toluene or application of second lacquer coat over dried coat, or both.

d) Plasticized lacquer on primed-steel panels immersed in distilled water at 40°C for 100 hours, then panels rated according to ASTM test D-714.

e) Plasticized-lacquer films on glass panels exposed in Weather-Ometer* for 125 hours, then gloss measured (highest values are best).

*Trademark of Atlas Electric Devices Co.

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EPOXY RESINS

Epoxy resins generally are chemically resistant, flexible, tough, and adhesive. Available as solids, liquids, or solutions, they are useful in surface coatings, including chemical-resistant coatings, maintenance coatings, baking finishes, and laminates; in adhesives; and in encapsulation, potting, lamination, and casting compounds.

Plasticizers are not ordinarily used in epoxy resins when maximum performance is desired. Because of their high cost, however, epoxy resins are often highly filled. Diluents are also often added to reduce the viscosity of liquid epoxy resins, to make them easier to handle.

Performance evaluations of several Monsanto plasticizers and reactive diluents for epoxy resins are tabulated in Table II.

APPLICATIONS

Surface Coatings

In surface coatings, the use of AROCLOR 1254, AROCLOR 1260, or AROCLOR 1262 imparts excellent chemical resistance, especially to acids and alkalies; flame retardance; and economy. AROCLOR plasticizers should not be used where resistance to solvents is desired, since they are true plasticizers and do not combine chemically with the epoxy resin.

Adhesives

In adhesives, including polyamide-epoxy resin combinations, evaluation of MOD-EPOX, AROCLOR 1254, and SANTICIZER 8 is recommended.

Encapsulation, Potting, Lamination, and Casting

For lower viscosity to aid processing, at lower costs, but with minimum change in physical properties, MOD-EPOX and SANTICIZER 8 are suggested for use in epoxy encapsulating, potting, laminating, and casting compounds. These reactive diluents react chemically with the resin so that the final properties are very similar to those of the unmodified resin.

Where additional softness or flexibility are desired, SANTICIZER 141 especially, SANTICIZER M-17, SANTICIZER B-16, AROCLOR 1221, SANTICIZER E-15, dibutyl phthalate, tricresyl phosphate, SANTICIZER 140, or AROCLOR 1248 may be used. On aging, some or all of this flexibility may be lost, depending on the temperature of exposure.

MONSANTO PLASTICIZERS

AROCLOR Plasticizers

The AROCLOR plasticizers are the most compatible of all the nonreactive plasticizers evaluated. Like epoxy resins, they impart excellent chemical and oxidation resistance and improved adhesivity.

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TABLE II—PERFORMANCE OF MONSANTO PLASTICIZERS AND REACTIVE DILUENTS IN EPOXY RESINS

Plasticizer[a,b]	Viscosity[c] Before Adding Curing Agent (cp)	Viscosity[c] After Adding Curing Agent (cp)	Physical Properties After Cure (0.5 hr @ 100°C) Izod Impact Resistance	Clarity; light reflected (%)	Hardness, Shore "D" (10 sec)	Physical Properties After Heat Aging (24 hours @ 87°C in activated carbon) Hardness Shore "D" (10 sec)	Weight Change (%)
None (control)	12,800[d]	7900	0.2	3.0	78	86	—0.012
Dibutyl Phthalate	1550	1300	—	3.5	10	78	—0.734
SANTICIZER E-15	3050	2100	—	2.5	10	80	0.119
SANTICIZER M-17	3150	2450	—	3.0	6	85	—0.131
SANTICIZER B-16	2300	2000	—	4.5	7	85	—0.013
Tricresyl phosphate	3750	3000	—	3.5	15	86	—0.222
SANTICIZER 140	2850	2200	—	3.5	22	79	—0.284
SANTICIZER 141	1500	1400	—	4.0	5	82	—0.425
AROCLOR 1248	7700	4300	0.6	3.0	40	88	—0.682
AROCLOR 1221	1650	1200	—	3.0	8	81	—2.118
MOD-EPOX	1650	1250	0.8 - 0.9	4.0	84	88	0.134
SANTICIZER 8	7600	3100	0.2	3.0	84	88	—0.007

a) Formulation

Ingredients	Parts
Epoxy Resin	100
Plasticizer	25
Tetraethylenepentamine	8

b) All are compatible in the liquid resin and in the cured resin; both at room temperature and after 0.5 hour at 100°C

c) Brookfield LVF #4 spindle; 60 rpm unless otherwise specified

d) 30 rpm

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Flammability and cost—two major limitations of epoxy resins—are diminished through the use of AROCLOR compounds: nonburning compositions are made by the use of an AROCLOR compound (15 PHR) and antimony oxide (5 PHR). About one-fourth the cost of epoxy resins, AROCLOR plasticizers permit significant cost reduction.

The use of the liquid AROCLOR plasticizers (1221 and 1248) in aliphatic amine-cured epoxies also improves flexural strength and compressive-yield strength, has little effect on tensile strength, and only slightly lowers heat-distortion temperature and ultimate compressive strength. They are commonly used in solventless coatings.

Solid AROCLOR compounds (1262 and 5460) greatly improve compressive strength, compressive-yield strength, flexural strength, and tensile strength; although they slightly lower the heat distortion temperature. They are used, sometimes in combination with liquid AROCLOR plasticizers, in solvent-containing coatings.

Extension of epoxy-resin adhesives with AROCLOR compounds greatly reduces the formulation cost and has minimum effect on the bonding characteristics of the adhesive.

MOD-EPOX

Ordinary reactive diluents reduce the viscosity of epoxy resins and thereby improve handling characteristics and permit the use of higher filler contents. Since they react with the curing agent and cost more than the epoxy resins, however, they generally tend to increase the cost of the formulation.

MOD-EPOX, by contrast, not only reduces the viscosity of liquid epoxy resins by as much as 75 per cent but also speeds cure, reduces curing-agent requirements by about one-third, improves bond strength of adhesives, and maintains hardness and other chemical and physical properties. Since it costs much less than any epoxy resin and any other reactive epoxy modifier, and since it lowers the curing-agent requirement, the incorporation of MOD-EPOX generally lowers the formulation cost greatly. Furthermore, MOD-EPOX is not a skin irritant like many other reactive diluents.

SANTICIZER 8

SANTICIZER 8 is another reactive diluent that effectively lowers the viscosity of epoxy resins and decreases the curing-agent requirement, without detriment to physical properties except for heat-distortion temperature.

A major, new unique benefit of the use of SANTICIZER 8 is that the polyamine curing agent can be diluted in it for easier handling and more accurate metering. The use of solutions of curing agent in SANTICIZER 8 should help to eliminate measuring errors and thereby reduce the frequency of overcured or undercured batches of epoxy resins.

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POLYESTER RESINS

Fiberglass-reinforced polyester resins are widely used for the manufacture of industrial and consumer products because of their high strength-to-weight ratio, ease of fabrication of large and complex forms, and chemical resistance. Molded articles, including buttons, are also made of polyester resins.

Although polyester resins are most often not plasticized, modification of their physical properties by plasticizers is desirable for some applications. Some of these modifications, and the appropriate Monsanto plasticizers that best impart them, are as follows:

Flame-retardance	AROCLOR 1260, 4465, and 5460
Flexibility	SANTICIZER 160, AROCLOR 1260, 4465, and 5460
Resilience	SANTICIZER 160
Moldability, gloss, and moisture resistance	SANTICIZER 9
Faster processing, clarity	Triphenyl phosphite
Initiator carriers (for easier, safer handling)	Dimethyl phthalate, Dibutyl phthalate, Tricresyl phosphate, and SANTICIZER 160

MONSANTO PLASTICIZERS

AROCLOR Plasticizers

The highly chlorinated, low-volatile, solid AROCLOR plasticizers, such as AROCLOR 1260, 4465, and 5460, are very effective and economical flame retardants for polyester resins, and they can increase the flexibility of the resin. Flame-retardant combinations of equal quantities of an AROCLOR compound and antimony oxide act synergystically; the AROCLOR compound imparts self-extinguishing properties to the resin, and antimony oxide reduces after-glow.

The use of an AROCLOR compound to impart flame retardance to a polyester resin offers the added advantage of eliminating the need for a higher-cost flexibilizing polyester, since the AROCLOR compound increases the flexibility of the naturally brittle resin. At 10-per cent concentration (enough, with an equal amount of antimony oxide, to make the polyester resin self extinguishing) these three AROCLOR compounds have from slightly less to slightly more effect on flexural strength and on flexural modulus of a reinforced polyester than a flexibilizing polyester does. At 20-per cent concentrations, each of these AROCLOR compounds increases the impact strength of the polyester resin, whereas the flexibilizing polyester decreases it.

SANTICIZER 160

The use of SANTICIZER 160 as an external plasticizer in polyester resins increases flexibility and resilience (U. S. Patent No. 2,757,158, J. R. Darby and A. R. Hempel, assigned to Monsanto Chemical Company). Cast sheet consisting of from 15 to 50 parts SANTICIZER 160 per 100 parts unsaturated polyester resin and 37.5 parts styrene is hard, tough, and resilient; whereas similar sheet without SANTICIZER 160 is hard and tough, but very brittle.

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SANTICIZER 9

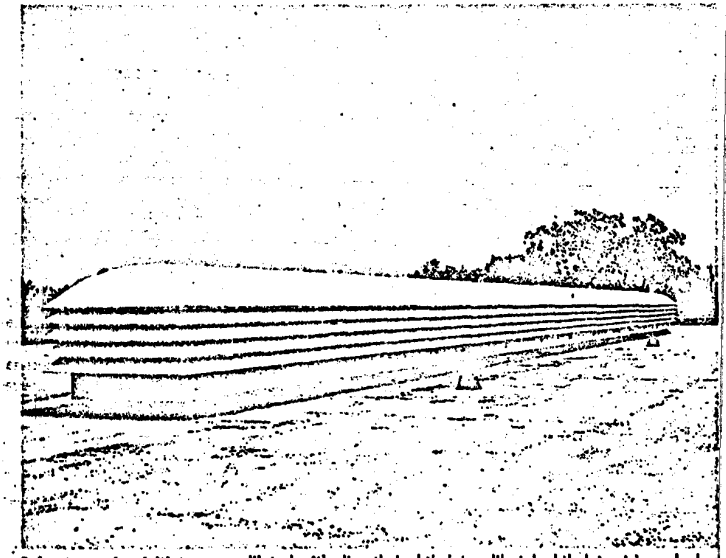
SANTICIZER 9 improves processability of polyester molding compounds and also imparts gloss and moisture resistance to molded products, such as buttons.

Catalyst/Clarifier—Triphenyl Phosphite

In the presence of a small amount of Monsanto triphenyl phosphite, the processing time of polyester and alkyd resins is shortened—and lighter, clearer products are obtained. For example the processing time for a maleic anhydride-ethylene glycol polyester resin was reduced from 95 to 80 minutes, and the final resin color was improved from APHA 20 - 25 to APHA 15 - 20 by the addition of 0.5-per cent triphenyl phosphite.

Peroxide-Initiator Carriers

Peroxide initiators ("catalysts") used in polyester-resin processing are more easily handled if diluted and desensitized by compatible plasticizers such as dimethyl phthalate, dibutyl phthalate, tricresyl phosphate, and SANTICIZER 160.



Polyester curing initiators are diluted with dimethyl phthalate, dibutyl phthalate, tricresyl phosphate, or SANTICIZER 160 for easier, safer handling. In polyester coatings, AROCLOR plasticizers impart flame retardance.

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NYLON

Plasticizers impart better low-temperature flexibility and improved impact resistance to nylon, increasingly important benefits since carbon black and other fillers tend to reduce these properties.

Monsanto's sulfonamide plasticizers and resins—SANTICIZER 1-H, SANTICIZER 3, SANTICIZER 8, SANTICIZER 9, SANTOLITE MHP, and SANTOLITE MS-80%—are useful as flexibilizers and modifiers for nylon. Performance evaluations of five of these plasticizers are compared in the following table:

TABLE III—EVALUATION OF PLASTICIZERS IN NYLON*

Plasticizer (25 PHR)	Stiffness at 77°F (psi)	Hardness (Shore "D")	Tensile Strength (psi)	Elongation (%)	Water Absorbed (%)	Resistance Solubles Lost (%)
None (control)	35,900	67	5700	320	2.00	0
SANTICIZER 1-H	11,560	27	3080	100	1.61	0
SANTICIZER 3	10,850	34	4930	480	0.94	0.16
SANTICIZER 8	12,700	40	1830	250	1.98	1.89
SANTICIZER 9	9,800	58[a]	3100	350	1.67[a]	1.30[a]
SANTOLITE MHP	5,790	28	3960	360	1.24	1.10

*Du Pont's Zytel 101 resin

a) 15 PHR

SANTICIZER 1-H

SANTICIZER 1-H is the most resistant plasticizer to extraction by water.

SANTICIZER 8

SANTICIZER 8, the best available plasticizer for nylon, aids processing by lowering the melting point. It imparts improved toughness, flexibility, and low-temperature flexibility to nylon without affecting other resin properties. SANTICIZER 8 is excellent for oil-resistant nylon coatings on fabrics and paper.

SANTICIZER 9

SANTICIZER 9 imparts a significant amount of flexibility to nylon with little reduction in tensile strength. Although blushing may occur at a plasticizer concentration of 25 per cent, a concen-

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tration of 20 per cent or less is usually sufficient for practical industrial uses. A patented composition* for precision casting, however, contains from 30- to 90-per-cent SANTICIZER 9 with either nylon 6-6 or nylon 6-4. Such compositions, when cured, have a Brinell hardness of 8 kg/sq mm (11,400 psi) and an impact strength of 8 to 10 kg/cm (45 to 56 lb/in.).

SANTOLITE MHP

As a useful extender resin, SANTOLITE MHP materially reduces the net cost of either molding or solvent nylon compositions, without detracting from their desirable properties.

OTHER POLYAMIDES

Polyamide surface coatings based on dimer acids and diamines adhere exceptionally well to paper, waxed glassine, waterproof cellophane, and plastics; and they have good flexibility. These polyamide resins are also used in printing inks, overprint varnishes, paint vehicles, and hot-melt coatings and adhesives. Polyamide suspensoids give good heat-seal bonds to other surfaces and enhance the water and grease resistance of paper.

Somewhat internally plasticized, polyamides need no added plasticizers for most applications. In hot-melt coatings and adhesives, though, external plasticizers are necessary. Strongly polar plasticizers, such as the sulfonamides, are extremely beneficial in these applicaations, since they impart tack, increase flexibility, improve gloss, and lower the softening and heat-sealing temperatures. Several typical polyamide-based adhesives formulations are the following:

POLYAMIDE ADHESIVES STARTING FORMULATIONS

Ingredients	Low-Temperature		Delayed-Tack	General-Purpose Hot-Melt	For Poly-ethylene	Book-binding[c]
	(parts by weight)					
Versamid ** 100 polyamide resin	—	—	—	—	100	—
Versamid 940 polyamide resin	100	100	100	100	—	100
SANTICIZER 8	—	—	—	10[b]	100	—
SANTICIZER 9	—	—	31.6[a]	—	16.6	—
AROCLOR 1254[d]	—	—	—	—	—	85
Dibutyl phthalate	12	11	—	—	—	—
Dicaprylhexyl phthalate	—	—	—	—	33.2	—
*Staybelite*** ester #10	6	—	—	10	—	—
Paraffin (m. 130°F)	—	—	—	4	—	—
Candelilla wax	—	—	5.9	—	—	—
Isopropanol	—	—	29.5	—	—	—
Toluene	—	—	29.5	—	—	—

a) With a higher concentration of SANTICIZER 9, the tack may be delayed for several hours.
b) SANTICIZER 8 increases the low-temperature flexibility
c) U. S. Patent No. 2,612,463, assigned to the Du Pont Co.
d) or AROCLOR 1242, 1248, 1260, or 1262

*German Patent No. 1,018,592, October 31, 1957, to Regie nationale des usines Renault
**Trademark of General Mills Corp.
***Trademark of Hercules Powder Co.

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MOLDING AND LAMINATING COMPOSITIONS

Brake Bands and Clutch Faces

SANTICIZER 9 is a valuable plasticizer and fluxing agent in the manufacture of molded phenolic-resin composition brake linings and clutch faces. By reducing the viscosity of the composition at molding and laminating temperatures, it improves flow properties. By helping to "wet" the fillers and abrasives, it helps produce a uniform mixture, which wears longer and more uniformly. Usually comprising from 5 to 10 per cent of the composition, it greatly improves flexibility.

AROCLOR 1268 and AROCLOR 2565 also improve flow properties and promote mixing and are useful in the manufacture of brake linings.

Punching Laminates

Several Monsanto plasticizers are often used to improve the cold-punching characteristics of phenolic-resin laminates. Tricresyl phosphate and the AROCLOR compounds also impart flame retardance. Because of the sharpness of punches when tricresyl phosphate is used, at a concentration of from 5 to 10 parts per hundred parts of resin, fewer finished parts are rejected. Tricresyl phosphate also imparts some flexibility. The higher-molecular-weight AROCLOR plasticizers (1262 and 5460) are often used for their flame retardancy.

Electrical parts molded of phenolic-impregnated and laminated paper often need added flexibility for cold or hot punching. Both SANTICIZER 160 and dibutyl phthalate have good electrical properties, and at concentrations of from 5 to 10 PHR, they impart suitable punching and flexing properties.

SANTICIZER 8 also imparts some flexibility, in addition to improving the cold-punching properties of phenolic laminates. *HB-40* is also useful in electrical punching laminates.

Composition Wallboard

As a mixing aid, SANTICIZER 9 is invaluable in promoting uniformity of phenolic composition wallboard.

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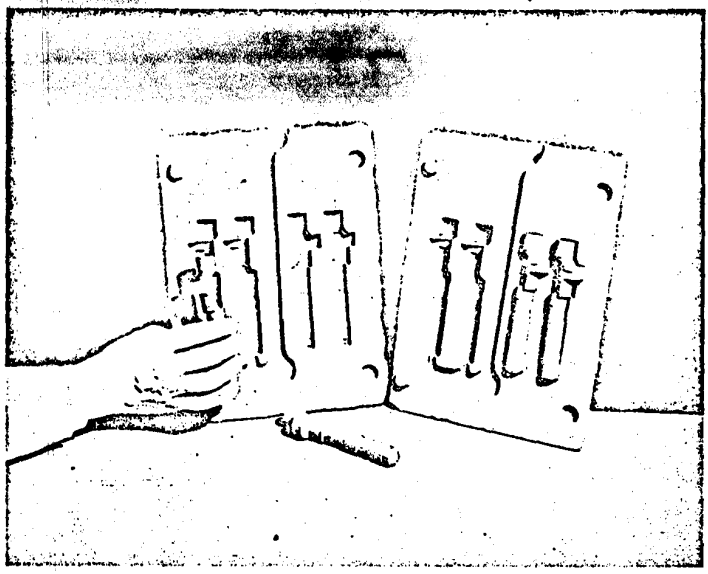

Phenolic-resin binders, plasticized with HB-40 or dibutyl phthalate, in foundry shell molds permit closer tolerances and smoother castings.

ADHESIVES

Phenolic clutch- and brake-lining adhesives, containing SANTICIZER 9 at a concentration of about 10 PHR, have potential applications. In various phenolic hot-melt adhesives, SANTICIZER 9 improves adhesion and flow of the resin.

SURFACE COATINGS

Phenolic surface coatings are most widely used in marine and masonry applications. In one phenolic marine varnish that performed well in a 14-month Florida weather-exposure test, AROCLOR 1268 imparts a velvety finish.

SANTICIZER 9 aids in mixing and in the achievement of uniformity in phenolic surface coatings.

PRINTING INKS

In phenolic resin-based inks, SANTICIZER 8 improves toughness and durability, and SANTICIZER 9 improves flexibility and printability.

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LAMINATES

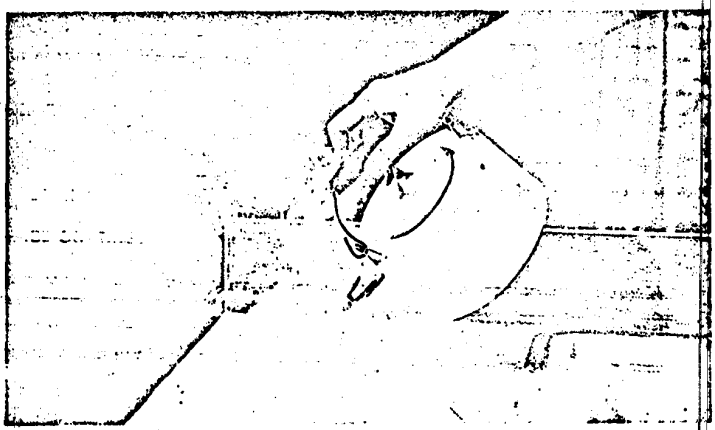
In melamine laminates, SANTICIZER 9 improves flow characteristics, imparts greater solution stability, and permits drying to lower moisture content. SANTICIZER 9 produces higher-gloss finishes in baking or curing operations by improving flowout and by minimizing pigment discoloration. SANTICIZER 9 also increases impact strength and abrasion resistance and improves buffability of the finished coating or laminate.

HIGH-IMPACT MOLDING COMPOUNDS

SANTICIZER 9 improves dimensional stability and reduces warpage, the two major problems of high-impact melamine molding compounds. It reduces shrinkage by permitting the molding powder to be made with a lower volatile content, and it reduces warpage by preventing development of some of the internal stresses.

INTUMESCENT, FIRE-RETARDANT COATINGS

A combination of either SANTICIZER 140 or tricresyl phosphate with either mono- or diammonium phosphate imparts flame retardance to melamine-urea-based intumescent coatings. SANTOLITE MHP is a useful plasticizer and flow aid.



In melamine laminates, SANTICIZER 9 produces higher-gloss finishes, improves buffability, and increases impact strength and abrasion resistance.

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CHLORINATED RUBBER

The performance of chlorinated rubber in coatings and in adhesives is usually enhanced by the presence of several Monsanto plasticizers, especially the AROCLOR compounds. Chlorinated rubber-based coatings, because of their resistance to corrosive agents, moisture, fungus, mold, and other deteriorating environments, are widely used on masonry floors, walls, and swimming pools; on chemical and food-processing plants; on railroad and marine equipment; and on highways, for traffic markings.

The AROCLOR plasticizers primarily increase resistance to acids, alkalies, salt water, and moisture; but they also impart adhesivity, improve cold-check resistance and weatherability, and make softer films.

Other Monsanto plasticizers useful in chlorinated-rubber coatings include SANTICIZER B-16, dibutyl phthalate, triphenyl phosphate, tricresyl phosphate, and SANTOLITE MHP.

AROCLOR plasticizers and dibutyl phthalate are used in chlorinated rubber-based heat-sealing adhesives that have chemical resistance and low moisture-vapor transmission.

STYRENE-BUTADIENE COPOLYMERS

Styrene-butadiene copolymers are widely used in enamels, maintenance finishes, exterior masonry paints, aluminum coatings, wall sealers, paper coatings, and printing inks.

The AROCLOR compounds are the most commonly used plasticizers for styrene-butadiene resins, but SANTICIZER B-16, SANTICIZER 160, dibutyl phthalate, dioctyl phthalate, and tricresyl phosphate are also useful.

NEOPRENE

AROCLOR plasticizers impart flame retardance to neoprene compositions. A small amount of AROCLOR 1268 added to neoprene imparts excellent working qualities for injection moldings. Neoprene modified with AROCLOR compounds is very useful as wire and cable coatings. AROCLOR 5460 imparts plasticization and adhesivity to neoprene-based protective and decorative coatings that are commercially used on rubber products.

POLYBUTENE

Mixtures of AROCLOR plasticizers and polybutenes make permanently tacky coatings for fabric or paper. Such coatings are used for tape and sign backing, refrigerator-sealing compounds, auto-body and windshield mastics, and foundry-core seals. Coatings containing insecticides make effective insect traps or barriers on tree trunks for foliage or fruit protection.

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Plasticizers are essential to modify many characteristics of nitrile rubbers. They improve processability, increase softness, reduce modulus of elongation, improve low-temperature properties, reduce volume change during immersion of vulcanizates, and lower the finished-product costs.

Monomeric esters, such as djbutyl phthalate, dioctyl phthalate, and dioctyl adipate are good softeners, have pleasant odors, and impart improved low-temperature properties. Polyesters, such as SANTICIZER 409 and SANTICIZER 411, impart good physical properties, low volatility, and resistance to extraction by oils and solvents.

Compatibilities of common plasticizers in nitrile rubbers are as follows:

Plasticizer	Compatibility (PHR)	Plasticizer	Compatibility (PHR)
Dibutyl phthalate	100	Dioctyl adipate	20[a]
Dioctyl phthalate	50	Diisodecyl adipate	33
Diisodecyl phthalate	33	Tricresyl phosphate	33
SANTICIZER 160	100	SANTICIZER 140	33
SANTICIZER 409	50	SANTICIZER 141	40
SANTICIZER 411	50	SANTICIZER B-16	50
		HB-40	50

a) incompatible in higher-molecular-weight nitrile rubbers

Performance of these plasticizers in nitrile rubber is compared in Table IV. Tensile strength, elongation, hardness, and modulus at 300- and at 500-per cent elongation are presented in Table V. Effects of aging (Table VI) and of solvent extraction (Tables VII and VIII) on these properties are also tabulated.

The adipates are the most efficient plasticizers for nitrile rubbers (especially on low-temperature flexibility), followed closely by dilsodecyl phthalate, dioctyl phthalate, and *HB-40*. SANTICIZER 140, SANTICIZER B-16, tricresyl phosphate, SANTICIZER 160, and dibutyl phthalate is the least-efficient group of plasticizers.

None of the plasticizers significantly affect either cure rate or tensile strength. The decrease in elongation is much less than the 50 per cent allowed by ASTM method 735-55T, and the hardness increase for all plasticizers is less than the 15 points allowed. Stocks containing any of these plasticizers meet the B-suffix requirement under ASTM method D735-55T (35 per cent maximum).

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TABLE IV—PERFORMANCE OF PLASTICIZERS IN NITRILE RUBBER[a]

Property	Dibutyl Phthalate	Dioctyl Phthalate	Diisodecyl Phthalate	SANTICIZER 160	Dioctyl Adipate	Diisodecyl Adipate	Tricresyl Phosphate	SANTICIZER 140	SANTICIZER 141	HB-40
Incorporation on Roll Mill (minutes)	18	19	18	20	20	19	16	18	18	19
Mooney plasticity										
Large rotor, 212°F										
Initial	89	90	86	100	83	83	94	98	98	86
1 minute	70	68	65	77	63	63	72	80	71	67
2 minutes	63	60	59	67	57	55	65	75	62	60
3 minutes	60	55	56	62	53	52	61	67	58	58
4 minutes	58	53	53	58	50	50	59	62	56	56
5 minutes	58	53	52	57	50	50	58	59	54	55
Compatibility (surface description: hung in air 36 days)	Dry	Dry	Dry	Dry	Very slight tack	Very slight tack	Slight tack	Very slight tack	Dry	Very slight tack
Low-temperature flexibility										
5 hours, —40°F	Flexible	Flexible	Flexible	Flexible	Flexible	Flexible	Flexible	Flexible	Flexible	Flexible
5 hours, —65°F	Stiff	Stiff	Stiff	Stiff	Flexible	Flexible	Stiff	Stiff	Stiff	Stiff
Compression set, % Cure, 45 min., 310°F ASTM Method B, 70 hr., 212°F	27.9	30.6	30.6	27.9	27.9	28.8	27.2	27.2	26.5	29.2

a) Formulation:

Ingredients	Parts by Weight
*Hycar** 1042 nitrile rubber	100
Plasticizer	15
FEF black	50
Zinc oxide	5
Stearic acid	1
*Thiurad*** activator	0.8
*Sulfasan*** anti-aging compound	0.8

cure: 20 min. at 310°F

*Trademark of B. F. Goodrich Co.

***Thiurad* and *Sulfasan* are trademarks of Monsanto Chemical Co., registered in the U. S. Patent Office.

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TABLE V—EFFECT OF PLASTICIZERS ON PHYSICAL PROPERTIES OF NITRILE RUBBER[a]

Plasticizer (15 PHR)	Modulus at 300% Elongation (psi)	Modulus at 500% Elongation (psi)	Ultimate Tensile Strength (psi)	(%) Elongation	Hardness (Shore "A")
Dibutyl Phthalate	1100	2070	2210	570	52
Dioctyl Phthalate	1130	2100	2220	560	54
Diisodecyl Phthalate	1170	2060	2310	590	54
SANTICIZER 160	1200	2265	2400	565	55
Dioctyl Adipate	1030	2110	2280	565	52
Diisodecyl Adipate	970	2070	2280	595	52
Tricresyl Phosphate	1290	2370	2540	600	57
SANTICIZER 140	1240	2280	2420	560	57
SANTICIZER 141	1150	2180	2360	575	56
SANTICIZER B-16	1260	2280	2400	575	56
HB-40	1150	2170	2320	575	56

a) Formulation and curing: same as for Table IV

TABLE VI–EFFECT OF PLASTICIZERS ON AGING OF NITRILE RUBBER[a]
(After aging for 70 hours at 212°F)

Plasticizer (15 PHR)	Modulus at 300% Elongation (psi)	Ultimate Tensile Strength (psi)	Elongation (%)	Hardness (Shore "A")
Dibutyl Phthalate	2040	2930	435	67
Dioctyl Phthalate	1850	2770	450	61
Diisodecyl Phthalate	1760	2700	450	60
SANTICIZER 160	1870	2830	450	63
Dioctyl Adipate	1870	2780	445	60
Diisodecyl Adipate	1770	2675	455	59
Tricresyl Phosphate	1910	2890	460	62
SANTICIZER 140	1920	2710	415	64
SANTICIZER 141	1790	2850	455	62
SANTICIZER B-16	2030	2700	450	63
HB-40	2040	2910	420	68

a) Formulation and curing: same as for Table IV

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TABLE VII—EFFECT OF PLASTICIZERS ON OIL RESISTANCE OF NITRILE RUBBER[a]

(After immersion in #1 ASTM Oil for 70 hours at 212°F)

Plasticizer (15 PHR)	Modulus at 300% Elongation (psi)	Modulus at 500% Elongation (psi)	Ultimate Tensile Strength (psi)	Elongation (%)	Hardness (Shore "A")	Volume Change (%)
Dibutyl Phthalate	1630	——	2775	495	55	—7.0
Dioctyl Phthalate	1540	2820	2900	530	55	—7.0
Diisodecyl Phthalate	1630	2750	2750	500	55	—6.9
SANTICIZER 160	1730	2860	2860	500	55	—5.8
Dioctyl Adipate	1580	——	2725	480	58	—7.3
Diisodecyl Adipate	1520	2725	2725	500	58	—6.8
Tricresyl Phosphate	1760	2860	2860	500	58	—4.6
SANTICIZER 140	1725	2860	2860	500	55	—5.1
SANTICIZER 141	1680	2890	2950	515	55	—5.8
SANTICIZER B-16	1720	2740	2740	500	58	—6.1
HB-40	1560	2780	2780	500	59	—7.4

a) Formulation and curing: same as for Table IV

TABLE VIII—EFFECT OF PLASTICIZERS ON OIL RESISTANCE OF NITRILE RUBBER[a]

(After immersion in #3 ASTM oil for 70 hours at 212°F)

Plasticizer (15 PHR)	Modulus at 300% Elongation (psi)	Modulus at 500% Elongation (psi)	Ultimate Tensile Strength (psi)	Elongation (%)	Hardness (Shore "A")	Volume Change (%)
Dibutyl Phthalate	1210	2320	2550	555	46	+7.5
Dioctyl Phthalate	1250	2350	2490	535	46	+6.3
Diisodecyl Phthalate	1230	2360	2430	520	46	+7.2
SANTICIZER 160	1370	2500	2500	500	46	+8.3
Dioctyl Adipate	1200	2370	2460	515	46	+7.2
Diisodecyl Adipate	1140	2370	2510	535	46	+7.0
Tricresyl Phosphate	1420	2620	2700	510	49	+9.0
SANTICIZER 140	1250	2530	2640	540	46	+8.7
SANTICIZER 141	1320	2480	2530	510	46	+8.5
SANTICIZER B-16	1370	2520	2570	515	48	+7.5
HB-40	1220	2360	2520	535	48	+7.4

a) Formulation and curing: same as for Table IV

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POLYSULFIDE RUBBERS

*Thiokol** polysulfide liquid polymers are easily converted "in place" to rubbery materials. Cured polysulfide rubbers are noted for outstanding oil and solvent resistance, excellent weatherability (oxygen, ozone, and light), good electrical insulation properties, resilience, and broad service-temperature range. They are used in sealants, casting and potting compounds, adhesives, and coatings—often in combinations with epoxy or phenolic resins.

Several Monsanto plasticizers and modifiers enable the formulator to obtain the benefits of these useful materials at economical costs.

Joint-Sealant Compounds

Polysulfide-based adhesives are increasingly used as joint sealants in curtain-wall construction and in airport runways. They are also widely used in jet fuel-resistant coatings and in skid-resistant surfaces on bridges and highways. Liquid AROCLOR compounds, such as AROCLOR 1232, are excellent viscosity- and cost-reducing modifiers, at concentrations of about 15 PHR, for sealant compounds.

Casting Compounds

Since they do not swell when in contact with solvents, polysulfide-based casting compounds are well suited for printing-press rolls, solvent-resistant gaskets, and similar cast products. Either dibutyl phthalate or an AROCLOR plasticizer may be used at a concentration of about 40 PHR to modify polysulfide casting compounds. Liquid AROCLOR compounds lower casting viscosity and raise filler tolerance, whereas the solid AROCLOR compounds are used where the lowest volatility is required.

Polysulfide-Epoxy Combinations

MOD-EPOX is used to reduce the viscosity of uncured polysulfide-epoxy resin mixtures for easier handling. It also increases the bond strength, reduces the curing-agent requirements, and lowers the overall costs, without adversely affecting other properties of the compound.

AROCLOR plasticizers, *HB-40*, and SANTICIZER 8 are also used in polysulfide-and-epoxy-based concrete-patching formulations and adhesives to reduce viscosity and lower cost.

SILICONE RUBBER

AROCLOR compounds are very effective flame retardants for silicone rubbers.

CREPE RUBBER (NATURAL)

AROCLOR 1262 is used as a low-cost plasticizer for crepe rubber in paint compositions. In concentrations of from 5 to 50 per cent of the weight of the rubber, the AROCLOR plasticizer increases alkali resistance, gloss, and adhesivity to steel.

*Trademark of Thiokol Chemical Co.

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POLYVINYLIDENE CHLORIDE

Vinylidene chloride homopolymers and copolymers have excellent chemical resistance and low moisture-vapor- and gas-transmission rates. In some applications no plasticizer is needed, but in textile and paper coatings a plasticizer is required to impart the desired flexibility.

Since any plasticizer reduces chemical and moisture-vapor resistance, the selected plasticizer must be efficient. The phthalyl glycolates (SANTICIZER B-16, SANTICIZER E-15, and SANTICIZER M-17) are very efficient. So are SANTICIZER 141, SANTICIZER 160, dioctyl phthalate, and diethyl phthalate. Performance of several plasticizers in saran resin (vinylidene chloride-vinyl chloride copolymers) are shown in the following table.

TABLE IX —EVALUATION OF PLASTICIZERS IN SARAN[a]

	Relative Compatibility[b]		Volatility (87°C, 2 hr.) Plasticizer lost (%)		Solvency	
	5% Plasticizer	10% Plasticizer	5% Plasticizer	10% Plasticizer	Rating	Precipitation Temp. (°C)
SANTICIZER B-16	0	0	6.1	13.8	Hot Solvent	130
Dioctyl Phthalate	0	1	7.8	7.8	Hot Solvent	96
SANTICIZER 160	1	2	5.7	12.4	Hot Solvent	92
SANTICIZER E-15	1	0	10.1	18.0	Non-Solvent	—
SANTICIZER 213	4	4	5.3	11.8	——	—
AROCLOR 5460	5	0	4.6	0.7	——	—
SANTICIZER 141	8	7	7.1	10.7	Hot Solvent	69

a) Saran resin B-118, Dow Chemical Co.
b) On a relative scale from 0 = no exudation to 10 = incompatible

Completely nontoxic SANTICIZER E-15 and SANTICIZER B-16 are excellent plasticizers for saran. In hot-melt, extruded-paper coatings, they aid in heat sealing and impart improved low-temperature flexibility. In solvent-cast saran-resin solutions, plasticizers impart improved flexibility and aid in solvent release. Generally, only small percentages of the plasticizer are required to produce a high degree of softness and elongation. For example, films containing 25-per cent SANTICIZER B-16 with saran F-120 resin have greater than 300-per cent elongation.

Vinylidene chloride latexes, such as Dow latex 744-B are used in paper coatings. Plasticizers are essential to laydown of continuous, pinhole-free films. Plasticizers that accelerate fusion of latex particles aid in giving a pinhole-free coating. Strongly solvating plasticizers aid in heat sealing. SANTICIZER 141 is excellent in these respects and is superior to both dioctyl phthalate and tricresyl phosphate. Plasticizers generally impart to vinylidene chloride latexes the same properties they impart to polyvinyl chloride resins.

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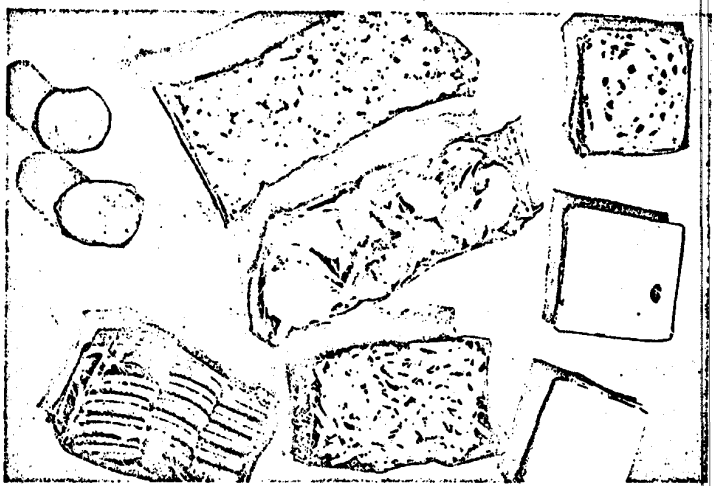

Efficient Monsanto plasticizers aid in heat sealing and impart flexibility, softness, and elongation to polyvinylidene chloride barrier coatings on packaging films.

A starting point for a clear coating for paperboard containers is as follows:

CLEAR COATING FOR PAPERBOARD CARTONS

Ingredients	% Solids	Dry (parts by weight)	Wet (parts by weight)
Dow Latex 744-B	50	100	200
SANTICIZER 141 emulsion[a]	50	18	36
Methocel[a] (15 cp.) methyl cellulose	5	0.6	1.2

	Parts by Weight
a) Phase A	
SANTICIZER 141	50
Oleic acid	3
Phase B	
28% Aqueous ammonia	1
Water	46

Phase B is added slowly to phase A during high-shear agitation. A water-in-oil emulsion forms first, and addition of more water phase inverts it into the desired oil-in-water emulsion.

[a]Trademark of Dow Chemical Co.

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A clear wallpaper coating can be produced with SANTICIZER 141 added without emulsification. A starting formulation is:

CLEAR, WASHABLE WALLPAPER COATING

Ingredients	Parts by Weight (dry)
Dow Latex 744 B	100
SANTICIZER 141	25
Syton* 200 colloidal silica	19

Scrub-resistant intumescent coatings for low-density fiber wallboard and acoustical tile are based on vinylidene chloride-vinyl chloride copolymer latexes. SANTICIZER 141 and dioctyl phthalate are the recommended plasticizers for such coatings. A suggested starting formula is as follows:

INTUMESCENT COATING

Ingredients	Parts by Weight (wet)
Part I	
Monoammonium phosphate	300
Dicyandiamide	53
Pentaerythritol	120
Titanium dioxide (rutile)	65
Water	235
Part II	
Dow Latex 744-B (50% solids)	200
Methocel (50 cp) (5% solids)	13.5
SANTICIZER 141 (or dioctyl phthalate)[a]	33
*Santomerse** 85[a]	5.8
Water[a]	27.5

a) The plasticizer is emulsified by adding the wetting agent to it and mixing vigorously while slowly adding the water.

The solvating, plasticizing, or swelling action of liquid plasticizers on the polymer at room temperature seriously reduces the mechanical stability of the latex. Solid plasticizers, such as diphenyl phthalate, triphenyl phosphate, and SANTICIZER 9, however, can be added to part I before milling, since they do not exert any solvating effect until the temperature exceeds their melting point (U. S. Patent No. 2,917,476).

The amount of solid plasticizer recommended is from 5- to 25-per cent of the polymer solids. The resulting coating has the abrasion resistance, scrub resistance, and fire-retardancy desired.

*Syton and *Santomerse* are Monsanto Chemical Company trademarks, registered in the U. S. Patent Office.

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POLYVINYLPYRROLIDONE

Polyvinylpyrrolidone is a water-soluble, film-forming resin that when unmodified dries to form hard, clear, transparent, glossy films. Compatible plasticizers may be added to alter hardness, to control tack or brittleness, and to decrease hygroscopicity.

Compatibility limits of several plasticizers in polyvinylpyrrolidone are as follows:

Plasticizer	Compatibility (PHR)
Dimethyl Phthalate	100
SANTICIZER E-15	100
SANTICIZER 141	33
SANTOLITE MHP	11

Essentially tack-free films at any relative humidity are obtained by the addition of 10-per cent SANTOLITE MHP. Dimethyl phthalate functions at a relative humidity of as high as 70 per cent, whereas SANTICIZER E-15 is an effective plasticizer at relative humidities lower than 50 per cent.

A more important use for plasticizers is in vinylpyrrolidone-vinyl acetate copolymers. Some of the end uses are in pressure-sensitive adhesives, rewettable adhesives, hair-grooming agents, white shoe polishes, and antitarnish coatings.

Monsanto plasticizers compatible with vinylpyrrolidone-vinyl acetate copolymers include:

dimethyl phthalate
dibutyl phthalate
SANTICIZER B-16
SANTICIZER E-15
SANTICIZER 141
SANTICIZER 213
SANTOLITE MHP

Generally 1:1 ratios of copolymer and compatible plasticizers yield adhesive, tacky, pressure-sensitive films. Such compositions adhere to polyester film, cellophane, cellulose acetate, kraft paper, urethane sponge, aluminum foil, glassine, and saran. Excellent adhesive coatings with good adhesion to glass, aluminum, and nylon are the following suggested formulations:

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FORMULATIONS FOR PRESSURE-SENSITIVE-ADHESIVE COATINGS

Ingredients	Plastisol (parts by weight)	Organosol (parts by weight)
Vinylpyrrolidone-vinyl acetate copolymer[a]	100	100
Opalon[*] 440 PVC resin	300	—
Vinylite[**] VYHH PVC resin	—	100
Dioctyl phthalate	200	15
Methyl ethyl ketone	—	200
Toluene	—	200

a) I-535, General Aniline & Film Corp.

To improve flexibility and reduce hygroscopicity, dimethyl phthalate may be added to hair grooming formulations (10- to 25-per cent based on resin solids). The following formulations are typical:

SUGGESTED HAIRGROOMING FORMULATIONS

Ingredients	Wave Set	Woman's Hair Spray (parts by weight)	Men's Hair Dressing
Vinylpyrrolidone-vinyl acetate copolymer[a]	100	100	100
Dimethyl phthalate	—	2.5	2.5
SANTICIZER E-15	5 - 12.5	—	—
Lanolin derivative	2 - 5	12.5[b]	25[b]
Silicone fluid	—	6.25	—
Isopropyl myristate	—	—	500
Perfume	95	6.25	25
Ethanol (absolute)	—	372	1845
Ethanol (95%)	900	—	—
Propellant (difluorodichloromethane)	—	2000	10,000

a) E-735, General Aniline & Film Corp.
b) *Lanogel* 41, Robinson-Wagner Co.

Opalon is a Monsanto Chemical Company trademark, registered in the U. S. Patent Office
**Trademark of Union Carbide Corp.

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TOWOLDMON0005041



PROTEIN RESINS

Protein materials such as casein, zein, allyl starch, and soya protein require special plasticizers. The following Monsanto products are plasticizers for these materials:

Primary	Secondary
SANTICIZER 3	Triphenyl Phosphate
SANTICIZER 8	Tricresyl Phosphate
SANTICIZER 9	Dibutyl Phthalate
SANTOLITE MHP	SANTICIZER 160
SANTOLITE MS-80%	AROCLOR Compounds
	SANTICIZER B-16

CASEIN

Casein is a conjugated phosphoprotein obtained from milk. Its use in surface coatings has been fairly well established, mainly as a protective colloid, binder, and stabilizer for emulsion paints.

In some applications unmodified casein is used. In others, the casein is modified and dissolved in water; formaldehyde is added to form a film that, when dry, is fairly water resistant. Unmodified casein can be dissolved in water in the presence of a suitable alkaline medium such as ammonia, morpholine, or 2-amino-2-methyl-1-propanol. The use of these volatile alkaline agents to dissolve casein results in improved washability of the film when completely dry. In addition, dissolving the casein in ammonia improves the shelf life of casein solutions.

SANTICIZER 9, very compatible in casein coatings and adhesives, permits greater tolerance of formaldehyde without causing reversable gels. It also imparts some flexibility to the coatings. With SANTICIZER 9, casein coatings and adhesives are less viscous than those dissolved in ammonia alone. In addition, SANTICIZER 9 improves the smoothness of pigmented material. Molding powders containing casein (67 to 68 per cent), SANTICIZER 9 (20 per cent), formaldehyde (2 to 3 per cent), and water (10 per cent) are compression molded into buttons.

SANTICIZER 8 in casein improves flexibility, water resistance, gloss, and adhesion and is compatible in molding compositions to at least 50 PHR. SANTICIZER 8 (at a concentration of 67 PHR in an aqueous-ammonia solution of casein) provides excellent flexibility and scuff and grease resistance in grease-proof-paper coatings.

SANTICIZER B-16 and SANTOLITE MS-80% make satisfactory emulsions with casein.

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ZEIN

Zein, an aqueous-alcohol-soluble corn protein, is a high-molecular-weight polymer composed of amino-acid groups united by peptide linkages. Solutions of zein in organic solvents or aqueous systems are adaptable to a wide range of coatings, film, fiber, and ink applications.

The high proportion of amide and non-polar side chains accounts for its solubility in many organic solvents. The only industrially available protein soluble in organic solvents, it is soluble in the lower aqueous alcohols, glycols, and glycol ethers. Solvents for zein generally contain at least one functional group (hydroxyl, carbonyl, amide, or amine).

Secondary solvents (which do not dissolve zein but which enhance its solubility in a primary solvent) include lower ketones, aliphatic esters, chlorinated hydrocarbons, and the higher glycol ethers. They permit modification of such properties of zein solutions as evaporation rate and viscosity. They also promote compatibility with various plasticizers and resins.

Zein is insoluble in water but readily soluble in dilute aqueous solutions of strong alkalies (pH 9.5). Useful aqueous systems of zein are prepared with ammonium or sodium resinates and various synthetic detergents such as the alkyl aryl sulfonates.

Unlike other proteins zein is resistant to microbial attack. Films and coatings are tough, glossy, scuffproof, and grease resistant. Fibers have wool-like properties, high tensile strength, and notable resistance to acids, alkalies, and organic solvents.

Although zein is compatible with a number of resins and plasticizers, Monsanto's highly-polar sulfonamide plasticizers—SANTICIZER 3, SANTICIZER 8, SANTICIZER 9—and sulfonamide-formaldehyde resins—SANTOLITE MHP and SANTOLITE MS-80%—are considered the best available modifiers for zein. Blends of zein with plasticizers and natural or synthetic resins yield fusible compositions.

Alcohol solutions of plasticized zein and a compatible resin are particularly adaptable to use as label and overprint varnishes that are tough, glossy, and scuff resistant. SANTICIZER 3 is perhaps the best plasticizer available for zein, in which it is highly compatible. Formulations plasticized with SANTICIZER 3, sometimes in combination with SANTOLITE MHP or rosin derivatives, are useful as decorative lacquers, release coatings for pressure-sensitive tapes, and hot-melt adhesives.

SANTICIZER 8 improves flexibility, water resistance, gloss, and adhesion and is compatible to at least 50 PHR. In label varnishes it prevents curling of the label.

SANTOLITE MHP is compatible with zein and improves brilliance, adhesion, and moisture resistance of zein compositions. The incorporation of SANTOLITE MHP in protein compositions makes possible the use of plasticizers that are otherwise incompatible. Thus, fairly flexible compositions can be formed by the use of SANTOLITE MHP, plus SANTICIZER B-16 equal to about half the weight of SANTOLITE MHP.

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SANTOLITE MHP markedly reduces viscosity and gelling of solutions of zein in 80-per cent isopropanol—20-per cent toluene. It also improves water resistance of cast zein films.

Highly grease-resistant and grease-proof zein-based coatings can be applied to paper and paper board.

Zein or zein-resin mixtures dissolved in alcohol or glycol are excellent vehicles for flexographic, moisture-resistant, or heat-set inks to which zein imparts rapid solvent release, hot or cold scuff resistance, hardness, and excellent pigment binding. The stability of alcohol-based flexographic inks is greatly improved by addition of wetting agents to the zein vehicles before pigment milling. These inks strongly resist precipitation on absorption of atmospheric moisture.

Deaminated zein dispersed in aqueous ammonia and plasticized with either SANTICIZER 8 or SANTICIZER 9 is gaining acceptance as a vehicle for water-based inks.

Fusible resins, made by blending zein with other resins and SANTICIZER 8, may be either pelletized or powdered and mixed with fillers to form molding powders, or they may be dissolved in solvents to give coating solutions. Various zein coatings are grease proof, water resistant, and glossy; and they are applied to paper, glassine, cellophane, foils, and textiles (as sizing).

ALLYL STARCH

Substitution of the hydroxy-hydrogen atoms of the starch molecule by allyl groups produces allyl starch, which forms stable, cross-linked polymers. At least 20-per cent plasticizer is required to make the film flexible.

SANTICIZER 8 is compatible in proportions greater than 20 parts per 100 parts of resin and is used with allyl starch in furniture finishes and grease-proof paper.

The AROCLOR compounds are highly compatible and very efficient plasticizers for allyl starch. AROCLOR 1242 is mentioned in U. S. Patent No. 2,740,724 (assigned to the U. S. Dept. of Agriculture) as a suitable plasticizer for an allyl starch emulsion in a preferred pH range of 8 to 11.

A typical emulsion formulation is as follows:

Ingredients	Parts by Weight
Allyl Starch	100
AROCLOR 1242	25
*Triton** X-100	6.25
Ammonium Hydroxide (conc.)	4
Water	310

The emulsion is stabilized by addition of sodium tetrahydronaphthalene sulfonate (*Alkanol*** S).

*Trademark of Rohm & Haas Co.
**Trademark of the Du Pont Co.

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ASPHALT

The major benefits of Monsanto plasticizers in asphalt are to provide adhesion, tack, and flame retardancy.

AROCLOR 5460, at a concentration of 30 per cent, makes asphalt caulking, roof-coating, and sound-deadening-coating compositions self-extinguishing. It also imparts adhesion and quick tack.

AROCLOR 5460 and *HB-40* are used together with asphalt to make sealers for asphalt roads.

MONTAR compounds are also used to provide flame retardance. The MONTAR products are compatible with asphalt at ratios up to two parts for each part of asphalt. Both softening point and brittleness of the asphalt blend are increased as the concentration of MONTAR compound is increased. Blending is accomplished by thorough mixing, with heat if necessary.

MONTAR 4 contributes flame retardance at concentrations as low as 10 per cent with instantaneous flame-out above 30 per cent. Flames are "snuffed" by an intumescent layer that forms on the surface of the mixture.

Solutions of MONTAR 4 in molten asphalt were heated in a crucible until flames occurred (about 200° C). The times required for the flames to go out after removal of the burner are shown in Table X for various concentrations of MONTAR 4:

TABLE X—EFFECT OF MONTAR 4 ON ASPHALT FLAMMABILITY

Concentration of MONTAR 4 (%)	Flame-Out Time (seconds)
0	210
10	90
20	10-20
30	Instantaneous
50	Instantaneous
67	Instantaneous

SHELLAC

SANTICIZER 8 increases the flexibility and definitely softens shellac without impairing the adhesion of the resin. SANTICIZER 9 and SANTICIZER B-16 are also useful, although less effective than SANTICIZER 8.

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PLASTICIZER COUNCIL

Perhaps your toughest, most urgent problem is not mentioned in this bulletin. Or maybe the suggested solutions do not completely meet your specific requirements.

It may prove worth your while to present your problem and requirements to Monsanto's Plasticizer Council. With no obligation, you will obtain prompt attention; concentrated, experienced thought; skilled laboratory experimentation; thorough evaluation; and an unprejudiced recommendation.

There are many sound reasons why it will pay you to consider Monsanto's Plasticizer Council as an extension of your own technical facilities—as many major plastics processers regularly do. As the pioneer in the art, technology, and science of plasticizing, Monsanto is uniquely organized to develop and capitalize on a team of research experts in all aspects and phases of plasticizer performance.

Since Monsanto produces more different plasticizers and more different classes of plasticizers than any other company anywhere, the Plasticizer Council can (and always does) suggest the one best plasticizer system to meet your performance and cost requirements. You never need to worry about Monsanto promoting a particular plasticizer just because it happens to be a Monsanto specialty. Your best interests always govern our proposals.

As you well know, new resins are being developed at an astoundingly rapid rate. Plastics are being tailored for more and more applications, and their performance requirements are becoming tougher. Just as you keep ahead in your major areas of technical competence, so Monsanto stays out in front in plasticizers. When new and better plasticizers are developed, Monsanto is most likely to be first with the best.

The Monsanto system of assigning a team of researchers to all aspects of research on plasticizers, including new products, product and process improvement, and customer service, works to your definite advantage. Chemists working on your problem can bring to bear the latest research results and thinking, as necessary, as well as drawing on more than 30-years' accumulated experience and data. And their new-product and product-improvement investigations are conducted in an environment of keen awareness of and appreciation for practical industrial needs.

Whenever a new or better plasticizer system appears to be the key to the development of your new product, the improvement of your present product, or the solution to your processing problem, the experienced creativity of Monsanto's Plasticizer Council is at your service. For consideration of your problem, you may either contact the Monsanto sales representative who calls on you or write:

Monsanto Chemical Company
Plasticizer Council, Dept. PL-332
Organic Chemicals Division
800 North Lindbergh Boulevard
St. Louis 66, Missouri

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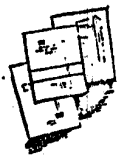

TECHNICAL BULLETINS ON MONSANTO PLASTICIZERS

Detailed technical information about the properties and applications of the Monsanto plasticizers mentioned in this bulletin is included in the following Monsanto technical bulletins. We revise these bulletins as often as necessary to include the most up-to-date and reliable information possible. We will promptly and cheerfully send you any bulletins you request.

Technical Bulletin No.	Title
Sulfonamides	
PL-1-H	SANTICIZER 1-H
PL-3	SANTICIZER 3
PL-8	SANTICIZER 8
PL-9	SANTICIZER 9
PL-320	SANTOLITE MHP and SANTOLITE MS-80%
Phthalyl Glycolate Esters	
PL-15	SANTICIZER E-15
PL-16	SANTICIZER B-16
PL-17	SANTICIZER M-17
Phosphate Esters	
PL-305	Tricresyl Phosphate
PL-301	Triphenyl Phosphate
PL-140	SANTICIZER 140
PL-141	SANTICIZER 141
Phthalate Esters	
PL-302	Dibutyl Phthalate
PL-312	Dicyclohexyl Phthalate
PL-303	Diethyl Phthalate and Dimethyl Phthalate
PL-300	Diisodecyl Phthalate
PL-318	Dioctyl Phthalate
PL-319	Diphenyl Phthalate
PL-160	SANTICIZER 160
PL-165	SANTICIZER 165
PL-213	SANTICIZER 213
Adipate Esters	
PL-308	Diisodecyl Adipate
PL-304	Dioctyl Adipate
Other Plasticizers	
PL-409	SANTICIZER 409
PL-411-D	SANTICIZER 411
PL-313	MOD-EPOX
PL-40	HB-40
PL-317	Triphenyl Phosphite
PL-328	MONTAR Compounds
PL-306	AROCLOR Plasticizers
PL-311	AROCLOR resins and plasticizers for chlorinated rubber
CS-14 (Chemical Specialties Data Report)	AROCLOR Fire-Retardant Plasticizers and Modifiers for Epoxy Resins
General	
PL-307	Monsanto Plasticizers in Synthetic-Resin Adhesives
PL-327	Monsanto Plasticizers in Protective Coatings
PL-331	Monsanto Modifiers for Thiokol Polysulfide Liquid Polymers

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THESE REPLY CARDS ARE FOR YOUR CONVENIENCE IN OBTAINING ADDITIONAL TECHNICAL INFORMATION

(date)

Gentlemen:

Please send me a copy of each indicated technical bulletin containing additional detailed information about Monsanto plasticizers for hard-to-plasticize resins:

PL_____ PL_____ PL_____

PL_____ PL_____ PL_____

Comments_____

Name_____

Title_____

Company_____

Address_____

City_____ Zone_____

State_____

(date)

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Title_____

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PLASTICIZER COUNCIL, DEPT. PL-332
Organic Chemicals Division
800 North Lindbergh Boulevard
St. Louis 66, Missouri

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Organic Chemicals Division
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PLEASE REQUEST SAMPLES ON YOUR COMPANY LETTERHEAD

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