Adhesive file

MONSANTO
CHEMICALS — PLASTICS

MONSANTO PLASTICIZERS
in Synthetic Resin Adhesives

Monsanto Technical Bulletin No. 0-99 April, 1953
Monsanto Chemical Company, Organic Chemicals Division, St. Louis 1, Mo.

INTRODUCTION

The superior properties of plasticized synthetic resin adhesives are causing these preparations to rapidly displace or supplement conventional animal and vegetable base adhesives. The synthetic resin adhesives referred to are primarily adhesives based on polyvinyl acetate and its co-polymers with polyvinyl chloride or polyvinyl alcohol, but also included are adhesives with such bases as nitrocellulose, rein, casein, acrylates, polystyrene, cellulose and other polymers.

Synthetic resin adhesives find a wide and increasing usage in such diverse industries as the following:

- Shoe industry
- Book binding industry
- Paper bag and folding box carton manufacturing
- Sanitary food container producers
- Laminators and converters of packaging products
- Tobacco industry (packaging)
- Automotive industry
- Food industry (for labels and carton sealing), etc.

Factors contributing to the rapid increase in the quantity use of synthetic resin adhesives are these:

1) Synthetics are better adapted to high speed machinery operation and make up their increased cost over other adhesive types by the resultant increases in production rates.

2) Synthetic adhesives are cleaner and easier to use from a production and maintenance standpoint.

3) Synthetic adhesives have superior water, mold and fungus resistance and better light stability than conventional organic adhesives. Also, any degree of flexibility can be obtained.

4) Adhesive emulsions obviate the use of volatile, toxic or flammable solvents. Emulsion properties can be carefully adjusted and controlled for specific needs.

Plasticizers are essential in synthetic resin adhesives for improving film formation, imparting tack, decreasing drying time, imparting flexibility and gloss and reducing costs. Production rates are [illegible] several hundred [illegible] from ordinary pastes and glues to synthetic resin adhesives. [illegible] are [illegible] [illegible] often used to [illegible] with [illegible]

[illegible]

MONSANTO PLASTICIZERS in Synthetic Resin Adhesives
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TYPES OF RESIN ADHESIVE FORMULATIONS

The major types of plasticized synthetic resin adhesive formulations are A, Emulsion; B, Hot-melt; C, Delayed-tack; D, Solvent; E, Pressure Sensitive and F, Adhesive Primers or Coatings. These will be discussed in order. Units for all formulations are weight percent or parts by weight. Sources of ingredients are listed at the back of this bulletin.

A. Emulsion Adhesives

Resin emulsion adhesives are emulsions of plasticized resins dispersed in a water base. They are often extended with materials like starch paste and thus require the incorporation of a preservative. The resin most commonly used in emulsion adhesives is polyvinyl acetate. The following is a typical polyvinyl acetate emulsion adhesive formula:

A.-1.	Polyvinyl acetate emulsion (55% solids)	100
	Plasticizer	10 -50
	Clay Filler	0 -30
	Cooked starch or dextrine	0 - 1,000
	Preservative	1 -2
	Stabilizer	1 -2
	Wetting Agent	0 -0.2
	Secondary water	75 -100
	Defoamer	1 -2
	Odorant (masking agent)	0 -1

The plasticizers most commonly used in polyvinyl acetate emulsion adhesives are dibutyl phthalate and ortho-nitrobiphenyl (ONB). Dibutyl phthalate imparts good flexibility and softening action with relatively low volatility. ONB is not quite as efficient as dibutyl phthalate as a plasticizer, but is widely used because of its economy as either an "extender" plasticizer or as the sole primary plasticizer.

Dimethyl phthalate is used in some cases because of its low cost and because it is a better solvent for bonding to cellulose acetate film or sheeting where this material is used in making windows in or laminations to paper. Tricresyl phosphate and Santicizer® 140 are used where flame resistance, oil resistance and low volatility are desired. Santicizer 140 is more efficient than TCP and has better light stability and less odor.

Santicizer M-17 is an excellent plasticizer for bonding acetate overlays to paper, because of its superior light stability. Santicizer 8 imparts good flow and wetting action and has excellent grease resistance. Santicizer 160 is considered better in some applications than dibutyl phthalate because of its lower volatility, greater film toughness and improved moisture resistance.

Santicizer products B-16, E-15 and 141 are used for nontoxic applications (food wrapping films, etc.) and have been granted approval for such uses by the U.S. Bureau of Animal Industry and the U.S. Food and Drug Administration.

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A. Emulsion Adhesives (continued)

Monsanto industrial resins, Santolite* MHP and MS-80%, are the best resin additives for use with polyvinyl acetate for imparting quick tack. They are being used successfully for bonding cellophane to cellophane and aluminum foil to paper. These resins make a very tough but flexible adhesive and are normally compounded with some liquid plasticizer like dibutyl phthalate, or with an eutectic mixture (1:1) of dibutyl phthalate and triphenyl phosphate.

The table on page 5 gives data evaluating various Monsanto plasticizers in combination with polyvinyl acetate. Properties evaluated are compatibility, volatility, low temperature flexibility and grease resistance.

It will be noted that the typical emulsion adhesive formulation A.-1 requires a preservative. Monsanto supplies an excellent line of industrial preservatives which includes Santobrite*, Santophen* 20, Milmer*I and these masking agents: methyl salicylate, Santomask*, saccharin, coumarin and vanillin. Literature on these products is available. At the back of this bulletin is a listing of the various trade marked products mentioned in succeeding formulas.

Formulas A.-2 and A.-3 below are more examples of polyvinyl acetate (PVA) emulsion adhesives.

A.-2. Quick Tack PVA Emulsion Adhesive

Gelva Emulsion S-56 (51% solids)	100
Dibutyl Phthalate	11.8
Santicizer* 8	11.8
Water	9.4

Through the use of other additives, adhesives designed for specialized purposes may be formulated. As an example, the following formulation shows good properties as an adhesive for bonding moistureproof cellophane to aluminum foil or to paper; or for bonding aluminum foil to paper.

A.-3. Polyvinyl Acetate Emulsion Adhesive

Gelva Emulsion S 55**	100
Dibutyl Phthalate	9
Santolite* MS-80%	13.5
Water	13.4

This formulation shows rapid development of adhesion and maintains good bond strength at elevated temperatures.

The following formula is an example of a low molecular weight styrene polymer emulsion adhesive.

*SANTOLITE, SANTOBRITE, SANTOPHEN, MILMER, SANTOMASK, SANTICIZER Reg. U.S. Pat. Off.
**See listing on page 8.

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A. Emulsion Adhesives (continued)

A.-4. Styrene Emulsion Adhesive

HB-40*	18.0
Diethyl Phthalate	6.0
Triton X155**	2.5
Lustrex* Styrene 601-40	100.0
Ammonia Caseinate, 15%	34.0

Formula A.-4. illustrates a basic, stable composition which possesses a high degree of wet tack. Such properties as stability, wet tack, and film toughness are imparted to this composition by the caseinate present and are varied by changes in the caseinate ratio.

The following formulation is suggested as a grease-resistant coating for paper products for wrapping such items as bakery goods.

A.-5. Polyvinyl Acetate Grease-resistant Paper Coating

Elvacet 81-900**	100
Santicizer* B-16	3.5
Tri-Pure **(titanium dioxide)	7.0
Water	15-30
Quilon**	0-5

The above composition is applied with a roll coater provided with a smoothing roll to develop a uniform continuous film. If used as a laminating adhesive, about 140°F. heat is required for optimum film formation.

B. Hot-melt Adhesives

Hot-melt adhesives may be made with either liquid or solid plasticizers, depending upon the properties desired in the end product. Santicizers* M-17 and 160 and dibutyl phthalate are favored because of their excellent heat stability and mild odor. Of the solid plasticizers, diphenyl phthalate and Santicizer 1-H are preferred because they have the least odor and are in the proper melting point range for most applications. Three formulations are given (all parts are by weight or in weight percent).

B.-1. Hot-melt Coating

Cellulose Acetate	50
Santicizer* M-17	88
Inert fillers	35

B.-2. Hot-melt Bookbinding Adhesive

Neville Hard Resin**	61.4%	Mix and heat
Santicizer 160*	15.0%	at 250°-275°F.
Paraffin wax	6.4%	until melted.

Raise temperature to 300°-325°F. and agitate after adding:

Vinylite AYAA (polyvinyl acetate)	12.9%
Ethyl cellulose	4.3%

B.-3. Bookbinding Hot Melt (application temp.: 165°175°F.)

Copolymer C-3	100
Aroclor* 1254	50-70
Dibutyl Phthalate or Santicizer 160	20-35
Clay	20-35
Fluxing resin (Bell-Ro or Rosin [illegible])	[illegible]

[illegible] AROCLOR, [illegible] LUSTREX [illegible]

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C. Delayed-tack Adhesives

These preparations, after they are spread and dried on a surface, are normally tack-free at ordinary temperatures. They are activated by heat and possess the property of maintaining tackiness over a fairly wide temperature range from several hours to several days. This permits the necessary mechanical handling, while two surfaces are being united, before the adhesive becomes nontacky by cooling and setting. Thus, the action of delayed-tack adhesives differs from that of hot-melt adhesives where tackiness terminates on cooling alone.

Solid plasticizers, such as diphenyl phthalate and Santicizers* 1-H and 9, make possible the "delayed-tack" feature of these unusual adhesives. Plasticizers are selected on the basis of their effect on the base resin (i.e., the temperatures at which the adhesive quality is activated and de-activated), and for their heat and light stability, odor, nontoxicity where required, etc. Much of this art is described in the patent literature (for example, U.S. patents numbered 2,462,029; 2,608,542; 2,608,543; 2,613,156 and 2,613,191) which should be investigated by those desiring to produce delayed-tack adhesives. Sample formulations below were taken from such patents, as indicated.

C.-1. **Example 9b Delayed-tack Adhesive** (from U.S. Patent No. 2,462,029)

Santicizer* 1-H	50
Vinsol Resin	50
Thinned Amine Dispersant	240
Acrysol M.R.	10

"The thinned amine dispersant is a mixture composed of 1 part stearic acid, 1 part "polypale resin", a polymerized rosin containing approximately 40% dipolymers of abietic acid (Hercules Powder Co.), 1 part of 2amino-2methyl-1 propanol (Commercial Solvents Corp.) and 3 parts of water. This composition is designed solely as a dispersing assistant . . ."

—From Column 10 of above patent.

C.-2. **Example 18 Delayed Tack Adhesive** (from U.S. Patent No. 2,462,029)

Diphenyl Phthalate	52.5
Nevindine R-3	30.0
Thinned amine dispersant (see above)	198.0
Hycar OR-25	43.5

The above formulation is nontacky at ordinary temperatures and is heat activated at about 150°F. The compound will then remain adhesive through temperatures as low as 50°F. Once set, the adhesive continues to hold at ordinary temperatures.

C.-3. **Polystyrene Emulsion Delayed-tack Adhesive**
(Example I of U.S. Pat. No. 2,613,156)

"Ten (10) parts polystyrene (molecular weight 10,000 - 15,000) and 40 parts diphenyl phthalate are mixed and heated together at approximately 190°F., forming a clear fluid. While still at this temperature, the fluid is poured into a solution of 6 parts of a 25% aqueous solution of Aerosol OT and 4.5 parts polyvinyl alcohol (of the grade sold under the trade name of Elvanol 50-42) in 75.5 parts water; the solution being at a temperature of approximately 190°F., constant agitation is maintained, resulting in a homogeneous emulsion. The emulsion is then permitted to cool." (This formulation is improved by the addition, after cooling, of 8 parts of Geon polyblend 550X20.)

This will form a smooth nongrainy film when spread evenly on paper and will dry to a completely tack-free surface. When heated to 170°F., the film becomes very tacky and powerfully adhesive, retaining these properties for as long as 70 seconds while cooling.

*SANTICIZER Reg. U.S. Pat. Off. Monsanto Product
See product listing on page 2.

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EVALUATION OF MONSANTO PLASTICIZERS IN COMBINATION WITH POLYVINYL ACETATE EMULSION

PLASTICIZER*	VOLATILITY 24 Hours at 87°C. (Activated Carbon)	LOW TEMP. FLEXIBILITY, °C. Modified Clash & Berg Test	OIL EXTRACTION — % Weight Loss After 24 Hours at Room Temperature		
			KEROSENE	PEANUT OIL	COTTON SEED OIL
Dimethyl Phthalate	5.6%	−1.6°C.	0.92%	0.75%	0.93%
Diethyl Phthalate	4.8	−5.0	0.85	0.63	0.82
Dibutyl Phthalate	4.4	−6.1	0.59	0.51	0.59
Diphenyl Phthalate	5.9	.....	1.31	0.90	0.98
Santicizer 160	2.1	+1.9	0.20	0.39	0.34
Tricresyl Phosphate	0.75	+3.6	0.16	0.38	0.46
Triphenyl Phosphate	2.0	+5.7	0.02	0.37	0.38
Santicizer** 140	1.2	+5.0	0.15	0.34	0.36
Santicizer 141	1.8	−3.3	0.17	0.42	0.31
Santicizer 8	3.6	+6.4	0.43	0.60	0.64
Santicizer 1-H	1.5	.....	0.96	0.36	0.53
Santicizer 9	3.1	.....	1.13	0.57	0.63
Santicizer B-16	2.2	−3.9	0.08	0.46	0.36
Santicizer M-17	3.6	+1.5	0.19	0.50	0.48
Ortho-Nitrobiphenyl	5.2	+3.7	0.69	0.72	0.68

*FORMULATION: 11 parts of plasticizer in 100 parts Shawinigan S-55 Gelva (polyvinyl acetate) emulsion. Film thickness 0.040 inches.

**SANTICIZER: Trade Mark Reg. U. S. Pat. Off.

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D. Solvent Type Adhesives

In this type of synthetic resin adhesive, solvents are used to carry the adhesive instead of water as in the emulsion type. Two typical formulations follow.

D.-1. **Heat Sealing Nitrocellulose Lacquer**

Nitrocellulose (½ sec.)	15%
Santolite* MHP resin	16%
Dibutyl phthalate	8%
Denatured alcohol	15%
Ethyl acetate	31%
Toluol	15%

Formulation D.-1 is suitable for bonding cellophane to cellophane or as a lacquer coating which can be heat sealed.

D.-2. **Nontoxic, Grease-resistant Paper Coating**

Vinylite VYHH**	80
Vinylite VMCH	10
Vinylite VAGH	10
Santicizer* 141 or M-17	20
Acetone	250
Methyl ethyl ketone	100

The above formulation can be used as a nontoxic, grease-resistant paper coating or heat sealing lacquer.

E. Pressure Sensitive Adhesives

These adhesives are tacky at ordinary temperatures and require moderate finger or roller pressure when placing coated materials.

E.-1. **Pressure Sensitive Adhesive** (calender onto fabric)

Cellulose acetate (Type A-9, Tennesee Eastman Corp., 40 mesh)	1
Santicizer 8	2.5 - 5
Santolite† MHP resin	1 - 2

E.-2. **Pressure Sensitive Adhesive** (calender onto fabric)

Vinylite AYAF (polyvinyl acetate)	5
Rauzene N100 (100% phenolic resin)	36
Santicizer B-16	18

E.-3. **Pressure Sensitive Adhesive** (hot-melt type)

Rubber or pale crepe rubber	15 - 25
Vistanex (polyisobutylene)	5 - 15
Santolite MHP resin	20
Ester gum	20
Methyl abietate, dibutyl phthalate, Aroclor* or Santicizer B-16	25 - 50
Wax (Montan, paraffin, carnauba or amorphous microcrystalline)	1 - 20

Melt all components except rubber at about 210°F. Add rubber and drop temperature to 180°F. Stir at this temperature for 1 to 2 hours until smooth. Hot cast on suitable surface.

F. Adhesive Primers

These preparations are used in the same fashion as paint primers; i.e., they are applied as a preliminary coating to make following coats adhere better. In this case, the follower coat may be any type of adhesive.

F.-1. **Adhesive Primer** (for bonding vinyls to paper or cloth)

Vinylite VYNS	18
Vinylite VMCH	2
Santicizer 160	15
Methyl ethyl ketone	25
Solvesso No. 1	17

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Miscellaneous Formulations

The following formulations are representative of the numerous synthetic adhesive preparations based on other than the polyvinyl acetate and PVA co-polymer resin bases mentioned in the introduction. Here a zein base is plasticized to give specialty products.

Zein Label Varnish

Zein	100
Rosin WW	100
Santolite MHP	20
Santicizer 8	25
Proprietary or 91% isopropyl alcohol	190

Zein Foil Tinting Base

Zein A	100
Santolite MHP	65
Santicizer 8	70
91% Isopropanol	230
85% Phosphoric Acid	2.3
Coloring	As needed

* * * *

Santicizers* 141, B-16 and E-15 are Monsanto plasticizers which have been given full approval by the U.S. Bureau of Animal Industry and the U.S. Food and Drug Administration for use in food wrapping films and other products where a nontoxic plasticizer is required. These Santicizers are particularly recommended for any adhesives which must meet similar requirements.

* * * *

LITERATURE AVAILABLE ON MONSANTO PLASTICIZERS

THE AROCLORS — Physical Properties and Suggested Applications: Technical Bulletin P-115.
AROCLOR* 1254 — Co-plasticizer With DOP: Technical Bulletin P-134.
DIOCTYL PHTHALATE (DOP): Technical Bulletin O-82.
HB-40*: Technical Bulletin P-104.
ORTHO-NITROBIPHENYL — Plasticizer and Chemical Intermediate: Technical Bulletin O-78.
ORTHO-NITROBIPHENYL — Toxicity Data: Technical Bulletin O-D-700.
SANTICIZER* 3: Technical Bulletin O-81.
SANTICIZER 8: Use in Adhesives; Use in Coatings; Use in Moldings: Three Separate Technical Data Sheets.
SANTICIZER 140: Technical Bulletin O-88.
SANTICIZER 141 The Nontoxic Plasticizer: Technical Bulletin O-D-114.
SANTICIZER 160: Technical Bulletin O-92.
THE BULK TANK STORAGE OF PLASTICIZERS: Technical Bulletin O-69.
FASTER PROCESSING OF POLYVINYL CHLORIDE WITH MONSANTO PLASTICIZERS: Booklet.
MONSANTO PLASTICIZERS In Polyvinyl Chloride Film and Sheeting: Technical Bulletin O-70.
An 80 page booklet entitled "Monsanto Plasticizers" presents much data and general information on the following products:

Dibutyl-, Diethyl-, Dimethyl- and Diphenyl Phthalates; Santicizers 1-H, 3, 8, 9, B-16, E-15, M-17, 140, 141 and 160; Tricresyl Phosphate and Triphenyl Phosphate.

This booklet is available on request.

OTHER MONSANTO LITERATURE ON RELATED PRODUCTS

SANTOBRITE* For The Preservation of Water Base Adhesives: Technical Bulletin O-1.
SANTOMASK* II For "After-Odor" Control of Interior Paint, Printing Ink and Other Odorous Compositions: Technical Bulletin O-16.
TRIPHENYL PHOSPHATE Application in Alkyd Resins: Technical Bulletin O-65.
BENTHAL* Application in Alkyd Resins: Technical Bulletin O-D-503.
SANTOLITE* MHP and MS-80% — Monsanto Industrial Resins: Technical Bulletin O-04.

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Listed below are the suppliers of special ingredients of the formulations presented in this bulletin. Most of the products are trade mark items.

MANUFACTURER	FORMULATION INGREDIENTS SUPPLIED
BAKELITE DIV., UNION CARBIDE AND CARBON CORP. New York, New York	VINYLITE vinyl resins.
BEACON CO. Boston, Mass.	MONTAN wax.
B. F. GOODRICH CHEMICAL CO. Akron, Ohio	HYCAR resins and rubber products.
E. I. DU PONT de NEMOURS & CO. Wilmington, Delaware	ELVACET polyvinyl acetate resins, TRI-PURE titanium dioxide opacifiers, QUILON resin insolubilizer.
ENJAY CO. (ESSO STANDARD OIL CO.) New York, New York	VISTANEX polyisobutylene resin.
ESSO STANDARD OIL CO. New York, New York	SOLVESSO aromatic solvents.
HERCULES POWDER COMPANY Wilmington, Delaware	VINSOL ROSIN WW and BEL-RO rosin products.
MONSANTO CHEMICAL CO. Plastics Division Springfield, Mass.	LUXTREX* heat resistant polystyrenes.
Organic Chemicals Division St. Louis, Missouri	SANTICIZERS 3, 8, 9, 107 (DOP), 140, 141, 160, 1-H, E-[illegible], B-16, M-17 resin plasticizers; SANTOLITES* MHP and MS-80% industrial resins; TRICRESYL PHOSPHATE, DIBUTYL-, DIETHYL-, DIMETHYL- and DIPHENYL PHTHALATES, TRIPHENYL PHOSPHATE and ORTHO-NITROBIPHENYL resin plasticizers; SANTOBRITE* water soluble preservatives; SANTOMASK* odor masking agent and coumarin and vanillin derivatives.
Phosphate Division St. Louis, Missouri	AROCLOR* plasticizers; HB-40* plasticizer.
NEVILLE CO. Pittsburgh, Pa.	NEVILLAC hard resin and NEVINDINE resin.
ROHM and HAAS CO. Philadelphia, Pa.	[illegible]
SHAWINIGAN RESINS CORP. Springfield, Mass.	

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AVAILABILITY OF MONSANTO PLASTICIZERS

Monsanto plasticizers are available in 55 gallon black iron drums and in full or compartment loads in tank cars and tank trucks. Because so many plasticizers are available from Monsanto, full advantage can be taken of the savings resulting from mixed shipments.

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New York, New York

BEACON CO.
Boston, Mass.

B. F. GOODRICH CHEMICAL CO.
Akron, Ohio

E. I. DU PONT & NEMOURS & CO.

ENJAY CO.
New York, New York

ESSO STANDARD CO.
New York, New York

HERCULES POWDER COMPANY
Wilmington, Delaware

MONSANTO CHEMICAL CO.
Plastics Division
Springfield, Mass.

Organic Chemicals Division
St. Louis, Missouri

MONSANTO
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For further information on the products described in this bulletin, contact the nearest Monsanto office.

MONSANTO CHEMICAL COMPANY

ST. LOUIS

AKRON • BIRMINGHAM • BOSTON • [illegible]
NEW YORK • PHILADELPHIA • [illegible]
CINCINNATI • CLEVELAND • [illegible]

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