SURVEY ON

PLASTICIZERS FOR ADHESIVES

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INTRODUCTION

The increased use of plasticizers due to the rapid growth of polyvinyl acetate in adhesive applications, the use of polyhydroxy alcohols to plasticize animal and vegetable glues, and the use of solid plasticizers in the relatively new fields of time-lag adhesives and hot melts indicated the need for a survey of the adhesive field. This survey covers that portion of the adhesive field that utilizes plasticizers, the properties required for these plasticizers and the potential growth in each application.

SUMMARY

A. Time-lag Adhesives

A relatively new field of growth for synthetic adhesives is the "time-lag" or "heat-sensitive" type adhesives for bottle labels, shoe adhesives and carton sealing tapes. Advantages of this type of adhesive include greatly decreased processing time and non-blocking properties. Solid plasticizers such as diphenyl phthalate (M.P. 69°C.), Santicizer 1-H (M.P. 86-87°C.), and Dow's P-7 (M.P. 103-105°C.) are being used since they most nearly satisfy requirements. However, a high melting plasticizer with better compatibility and a sharp melting point is required in the vast majority of the cases. The potential for solid plasticizers in this field is estimated to be approximately 20,000,000 pounds per year within the next ten years, at a price of 35 to 45 cents per pound.

B. Hot Melt Adhesives

Another large use for solid and liquid plasticizers is in hot melts. Once again, the properties desired for solid plasticizers indicate a high melting point with good heat stability and low toxicity for such applications as milk cartons, shoe adhesives and book bindings. The industry requirements for liquid plasticizers are satisfied by commercially available types.

C. Polyvinyl Acetate Adhesives

The use of polyvinyl acetate in adhesives was 11,000,000 pounds in 1949; this grew to 16,000,000 in 1950 and only the shortage during the first half of this year of monomer will prevent even greater use in 1951. This field will continue to grow. Four to five million pounds of plasticizer were required to plasticize the 16,000,000 pounds of resin used in 1950. Monsanto has a wide variety of plasticizers being used in this application -- orthonitrobiphenyl, dibutyl phthalate, dimethyl phthalate, tricresyl phosphate, and Santolite MHP. There is a trend toward lower-cost resinous-type plasticizers for these applications. Currently there is a wide variety

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of resinous plasticizers available for this market. Wider trade acceptance of the lower-cost resinous plasticizers offers a serious threat of reducing our plasticizer business in many applications.

D. Animal and Vegetable Glues

In 1950 9,370,000 pounds of polyalcohols were used to plasticize the approximately 350,000,000 pounds of animal and vegetable glues made in this country. These ranged in price from $0.17 for ethylene glycol to $0.44 for glycerine, with glycerine representing over 50% of the total. The trade desires a material that is less hygroscopic than those currently available. Due to the small percentage of plasticizer used, a lower price is not mandatory. Santicizer 132 and Santicizer 134 are being evaluated in this field.

CONCLUSIONS

A. The use of solid plasticizers for hot melt and time-lag adhesives is growing rapidly (20,000,000 pounds within ten years at 35 to 45 cents per pound). Currently available solid plasticizers are not entirely satisfactory.

B. Requirements for plasticizers in polyvinyl acetate adhesives will grow with a trend toward low-cost (less than 30 cents per pound) resinous plasticizers. These resinous plasticizers will not completely replace monomeric-type plasticizers, however.

C. The animal and vegetable glue industry needs a water-soluble plasticizer which is less hygroscopic than glycerine and Sorbitol. Potential for such a plasticizer is roughly 9,000,000 pounds per year and the price could be relatively high (40 to 65 cents per pound) since only small concentrations of plasticizers are used.

RECOMMENDATION

That we develop sharp-melting solid plasticizers (M.P. in the range of 70-100°C.) with better compatibility and efficiency than diphenyl phthalate and Santicizer 1-H for hot melt and time-lag adhesives to protect and enhance our position in this field.

DISCUSSION

A. Time-lag Adhesives

Time-lag adhesives for bottle labels, carton end-sealing tapes and shoe adhesives are now being offered commercially

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by Nashua Gummed and Coated Paper Company, S. D. Warren Company and Dennison Manufacturing Company. This type of adhesive depends on mechanically mixing crystals of solid plasticizer in resin and laying down a film on paper. Since the resin is not plasticized, it is non-tacky. When heat is applied to the coating, the plasticizer dissolves in the resin, plasticizing it, and the film becomes semi-permanently tacky even after cooling.

Patent number 2,462,029, dated February 15, 1949, by Lloyd M. Perry, assigned to Nashua Gummed and Coated Paper Company, broadly claims an adhesive made by a dispersion of discreet crystalline particles in resin that is activated by heat. When heated, the plasticizing properties of the crystalline solid are released providing an adhesive material. The feeling in the trade on the validity of this patent is varied. Several people feel prior art in the cellophane field invalidates the patent. Others either have been cautioned by Nashua or feel the patent is valid, for they are trying different approaches to the same problem.

Conventional glue labels block on storage (i.e. stick together due to high humidity) and require a long drying time after application. The advantages of time-lag adhesives over conventional glue labels include non-blocking during storage and faster plant processing time (60 bottles a minute for glue versus 350 a minute with time-lag adhesives.) This faster processing time has solved production lags that occured at the labeling machines in several plants.

This field has a tremendous potential for growth and will undoubtedly grow to large proportions within the next few years. Various consumers have indicated that within ten years the market for solid plasticizers in time-lag adhesives will be 20 million pounds a year.

At the present time Monsanto is in an excellent position on solid plasticizers for time-lag adhesives, offering both diphenyl phthalate and Santicizer 1-H. However, both of these plasticizers have deficiencies (compatibility, efficiency and migration tendencies) which must be overcome if we are to obtain the largest market potential.

The competitive situation on solid plasticizers for this application indicates that only Dow's P-7 (tri p-tertiary butyl phenyl phosphate) offers a serious threat at this time. This plasticizer, too, has certain technical deficiencies which need improvement.

The adhesive industry is interested in a solid plasticizer that has or imparts these properties to the adhesive:

1. The solid plasticizer should melt sharply between 80°C. and 90°C. (Desires range from 65°C. to 110°C.) This is

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important because compositions incorporating diphenyl phthalate become activated at too low a temperature, thereby causing blocking. Santicizer 1-H and dicyclohexyl phthalate (M.P. 58-65°C.) are worse than diphenyl phthalate in this respect.

2. Compatible with polyvinyl chloride, polyvinyl acetate, cellulose acetate, ethyl cellulose, Neoprene, GRS, coumarone-indene and esterified rosin. The means of measuring compatibility is to heat a mixture of resin and plasticizer together in a 1:1 and 1:3 ratio. On cooling, no immediate separation should be noted.

3. Supercool readily. Materials that supercool readily are usually satisfactory, but the reason is not fully known.

4. Slightly soluble in water and alcohol. Materials that are non-water soluble cause the bond between the label and the bottle to break on water immersion. Diphenyl phthalate is very poor in this respect, while Santicizer 1-H is somewhat better.

5. Low migration. Santicizer 1-H, and diphenyl phthalate to a lesser degree, have a tendency to migrate from the adhesive through the paper and lacquer and crystallize out on the opposite side of the label.

6. Better efficiency than diphenyl phthalate. Santicizer 1-H is satisfactory in this respect.

7. Toxicity at least as good as diphenyl phthalate and Santicizer 1-H.

8. Color of tan or better.

9. Emulsify readily.

10. Price. To gain widest and most rapid acceptance in this field, the price should be between 35 and 45 cents per pound.

Producers of time-lag adhesives desire plasticizers with these specific properties. Monsanto can undoubtedly develop a satisfactory solid plasticizer. Such a plasticizer would better our position in this field to a greater extent than if we continue to push only diphenyl phthalate and Santicizer 1-H.

B. Hot Melts

The hot melt method is a relatively new means of bonding materials which has excellent growth possibilities.

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Applications where hot melts are now being used or are being actively developed include adhesives for milk cartons, bookbinding and shoes. The milk carton adhesive is the most fully developed at this time. Synthetic adhesives are just starting to replace animal glues in the bookbinding field. The Battelle Memorial Institute has developed formulas based on polyvinyl acetate and coumarone-indene resins, plasticized with Santicizer 8, that are very effective. This is an excellent outlet for Santicizer 8 and should be pushed. The use of hot melts for shoe adhesives is as a replacement for rubber cements.

There is interest in both solid and liquid plasticizers for hot melts. Several commercially available liquid plasticizers are satisfactory, while the solid plasticizers have several deficiencies that must be overcome.

The properties that hot melt plasticizers should have are listed below:

1. Heat stability of at least 12 to 24 hours at 300-400°F. (In this test, dibutyl phthalate and Santicizer M-17 are acceptable, while diphenyl phthalate, triphenyl phosphate and tricresyl phosphate are not.)

2. The solid plasticizers should melt sharply between 60°C. and 110°C.

3. Low toxicity.

4. Less odor than diphenyl phthalate or dicyclohexyl phthalate upon heating.

5. Non-fuming at high temperatures.

Dicyclohexyl phthalate is quite widely used but has considerable odor when in the liquid state.

Once again the importance of developing new solid plasticizers to meet specific industry desires is emphasized. It is necessary for Monsanto to satisfy these desires or lose the position we now command with diphenyl phthalate and Santicizer 1-H.

C. Polyvinyl Acetate Adhesives

The use of polyvinyl acetate emulsion adhesives has been growing rapidly (11 million pounds of resin in 1949 - 16 million pounds in 1950). Consequently, the use of plasticizers in these adhesives has grown until it now consumes approximately

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4-5 million pounds of plasticizer a year. Indications are that it will continue to grow, but at a somewhat reduced rate.

Many of our plasticizers are now being used: ONB, dibutyl phthalate, dimethyl phthalate, tricresyl phosphate and Santolite MHP. However, the trend in the industry is towards low-cost resinous plasticizers which exhibit some tack themselves, such as Genseke's Synthol. To find the widest market, a new monomeric plasticizer for this field should sell for 25¢ a pound or less. Santicizer 180 and Santicizer 181 are being evaluated in this field because of their potential low cost.

A resinous plasticizer for polyvinyl acetate has a potential between one and two million pounds a year, if it is priced at approximately 30¢ a pound. If the price is lower, the potential will undoubtedly be greater. At the present time there are several resinous-type plasticizers that are currently being used. These are listed below:

Product	Cost per Lb. Delivered
Hercoflex 900	36.5
Polyco 438	35.0
Genseke's Synthol	24.75
Santolite MHP	44.0
Laminac	
Nevilac 10°	40.0
Resyl 41	
Non-oxidizing alkyds	
Phenolic terpene Types	20.0

While it would appear that the field is well saturated with resinous plasticizers, nearly all of these are relatively high in cost and could be replaced if a low-cost plasticizer could be developed.

Santolite MHP is a very good plasticizer for polyvinyl adhesives and confers properties highly desired by the trade. However, its high price limits its use. Consequently, to be in a better position for the long pull, it is suggested that we consider materials that will offer the same properties as Santolite MHP but at a much lower cost.

The properties desired in a plasticizer for polyvinyl acetate are:

1. Compatible at least in a 1:1 ratio with polyvinyl acetate.

2. Non-toxic, since many applications are for food packaging.

3. Good aging characteristics (volatility and light stability).

4. No migration tendencies.

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5. Good initial tack or grab to prevent carton flaps from springing open after pressure is removed.

6. Tasteless.

7. The plasticizer should be tacky itself (i.e. have some adhesive properties) and therefore add to the tackiness of the polyvinyl acetate emulsion.

8. Low cost. The cost should be 25¢ a pound or less.

Springfield is developing polystyrene latices in the adhesive field in direct competition with polyvinyl acetate. Since these also require plasticizer, the overall plasticizer requirements would be about the same.

D. Animal and Vegetable Glues

Animal and vegetable glues are currently consuming approximately 9,370,000 pounds of poly alcohols a year as plasticizers. Listed below is a breakdown on the relative importance and sales price of these individual poly alcohols in adhesives:[1]

Material	Amount	Price per Pound
Glycerine	5,000,000	44.0¢
Ethylene Glycol	1,500,000	17.0¢
Sorbitol	2,000,000	23.5¢
Diethylene Glycol	480,000	18.5¢
Triethylene Glycol	390,000	21.5¢
TOTAL	9,370,000	

As will be seen from this data, glycerine is the most important of these and commands a little over 50% of the business. Furthermore, glycerine is priced at $0.44 per pound during 1950 and represents a vulnerable market if a suitable non-hygroscopic water-soluble plasticizer can be developed to replace it.

In animal and vegetable glues, the poly alcohol required is only about two to three percent of the total glue. Consequently, the plasticizer can stand a relatively high price (40¢ to 65¢ per pound) since it reflects such a minor portion on the final cost. This price structure represents the opinion of U. S.

[1] Glycerine Producers Association Report for 1950

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Envelope and Paisley Products.

Water plasticizes animal glue. The use of a hygroscopic water-soluble plasticizer results in little control over the flexibility of the glue due to humidity changes. The desire for a non-hygroscopic plasticizer results from the curling of coated paper that is encountered in low humidity weather when a hygroscopic plasticizer is used. Both these problems are frequently encountered in envelopes.

The general properties of plasticizers for an animal and vegetable glue are:

1. Non-toxicity.

2. Impart good initial tack.

3. Plasticize over a wide humidity range without curling or sticking.

4. Effective in a low concentration to limit the humidity effect.

5. Tasteless.

6. Low cost.

7. Impart good flow and a film that will not contract or bubble on drying. This is for appearance only.

Santicizer 132 and Santicizer 134 are currently being evaluated by U. S. Envelope, Paisley Products and Stein-Hall as potential plasticizers for animal and vegetable glues. Hayes Adhesives' initial thinking is that triethylene glycol is more satisfactory than Santicizer 132 or Santicizer 134.

It is recommended that Research keep in mind the requirements of plasticizers for animal and vegetable glues. If any materials appear promising, they should be evaluated by a producer of glues.

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