Abstract of an article in May 1960 ADHESIVES AGE

SYNTHETIC HOT MELT ADHESIVES

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"Hot melts" are solid materials which become sufficiently fluid or tacky at elevated temperatures to be used as adhesives, coatings or binders. They have several advantages over adhesives or coatings applied as solutions or aqueous emulsions.

Essentially solid and immobile at temperatures below the flow temperature, hot melts impart excellent adhesion without requiring a porous or penetrable surface for releasing solvent or water. They have quick initial tack when molten, yet when cooled, harden rapidly with little shrinkage to give a strong bond. Toxicity and fire hazard problems associated with solvent systems are obviated; difficulties encountered when solvent or aqueous emulsion systems freeze are eliminated. In many cases, greater economy can be obtained with a hot melt system.

These features, particularly the ability to soften with heat yet solidify quickly when cooled, qualify hot melts for bonding and coating smooth surfaced materials such as foil, glassine, Mylar, cellophane and polyethylene. Excellent bonds are obtained simply by pressing a hot melt coated surface to another surface at the proper temperature.

The importance of hot melts to the adhesive user is exemplified by the mass production techniques used in today's packaging industry. Paper, foil, plastic and metal sheets are coated at rates of hundreds of feet per minute. Modern packaging machines can handle 100,000 or more units per hour. The coating or sealing operation is often the limiting rate factor.

Such high speed production requires adhesives or coatings which set rapidly, since the coated material must be ready for use or further processing immediately after being coated. There is not enough time usually to remove any solvent or water. The practically instantaneous bonding of hot melts is desirable and frequently indispensable.

Certain materials have been used as hot melts for centuries. Tar, wax, rosin and asphalt are examples of early and still widely used hot melts. The advent of synthetic resins and the use of laboratory tested principles in hot melt manufacture have quickened interest by industry. Hot melts have been "rediscovered" and their modern use is based on rapidly growing experimental programs by companies that make or use them. The situation is in many ways analogous to the "rediscovery" of the centuries' old aqueous emulsion paints and the growth of the technology.

Hot melts are prepared simply by "melting"together the lower melting components and adding the higher melting components at temperatures above their melting points.

Resins, waxes, plasticizers, fluxing agents, fillers, pigments, dyes and stabilizers are typical components of modern hot melt formulations. In our thinking, the basic ingredients in a hot melt is the polymeric film-forming resin such as polyvinyl acetate or polyvinyl butyral. These resins form a tough film base when the hot melt is applied and increase adhesion of the bond.

In general, they have very high viscosities in the molten state, i.e., at temperatures between 130° and 180°C. The high viscosities can be lowered greatly at these temperatures by incorporating lower molecular weight resinous "fluxing agents" such as rosin or coumarone-indene resins. Waxes and plasticizers are usually used in hot melts to impart proper flow of the coated film at temperatures suitable for heat sealing.

Plasticizers also improve flexibility and adhesion. Waxes add slip and non-blocking characteristics to the composition. Fillers and pigments are used when firmer films, opacity, color, or lower costs are desired. Antioxidants and stabilizers against the degradative effects of heat are required when the hot melts are held at elevated temperatures for extended periods.

Plasticizers -- The plasticizer is an important component in a hot melt. It largely influences film flexibility, melt temperature, flow and tack. We consider primary plasticizers to be generally compatible with the resin over the useful range of plasticizer/resin ratio.

Primary plasticizers for polyvinyl acetate are dibutyl phthalate, Kronisol, Santicizer 8, Santicizer 140, Sandicizer B-16, Santicizer 141, Pycal 94 and Resoflex 296. Primary plasticizers for polyvinyl butyral are dibutyl sebacate, butyl ricinoleate, dibutyl phthalate, Flexol 3GH and tricresyl phosphate.

Secondary plasticizers have limited compatibility with the resin and are used in combination with a primary plasticizer. They are used most often to lower costs, but do confer such specific properties as toughness, resistance to plasticizer migration in the film or improved control of hot melt viscosity. Dioctyl phthalate, Aroclor 1242 and Flexol 4GO are examples of secondary plasticizers.

Fluxing-Extending Resins -- As noted previously, hot melts based on polyvinyl acetate or polyvinyl butyral can be highly viscous and difficult to apply at a practical melt temperature. In some applications the cost may be prohibitive. Fluxing-extending resins are used to overcome these drawbacks.

A few fluxing-extending resins that are used with polyvinyl acetate and, in most cases, with polyvinyl butyral are:

Rosin WW	Polypale
Resin 861	Pentalyn A
Nevillac Soft	8L Ester Gum
Nevillac Hard	Petrex Wax
Arochem 650	Santolite MHP
Gum Dammar	Hercolyn
Vinsol	Belro
Staybellite	Pentalyn G
Abalyn	

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Extruders, kneading-type mixers, varnish kettles or other equipment providing intensive mixing and uniform heating are used to make hot melts commercially.

Extruders (single or double-screw type) are favored by manufacturers who desire to package a pelletized or rope-like product. In these forms, it is more convenient to feed to the coating machine and has a shorter remelt time. The ingredients are dry-blended, fed through a hopper into an extruder, cooled, pelletized and packaged. Extruders offer the advantage of short heating periods, which minimizes degradation and discoloration.

Kneading or masticating mixers (bottom discharge or tilting bowl models) are also used. The molten mix is poured into molds of convenient size or into strippable fiber drums for shipment, or is transferred directly to application equipment.

Simple varnish kettlesare adequate for making hot melts. Steel kettles equipped with slow speed stirrers fitted close to the bottom and sides are used. Dowtherm, hot oil, steam jacket or electric mantle can be used to obtain the desired temperatures, e.g., 300° to 400°F., for polyvinyl acetate based hot melts. Care must be taken to avoid localized overheating in order to prevent discoloration or degradation of the product.

A number of starting formulations have been developed and tested in our laboratory; many can be used with little further modification. Examples of hot melt adhesives and coatings based on polyvinyl acetate and polyvinyl butyral resins are given in the tables to illustrate the variety available. All components are given in parts by weight.

H-E11 is suggested as a starting point for developing hot melts which can be applied at 160° to 180°C. The plasticizer, Acrawax C and Nevillac resin are melted at 130°C. The polyvinyl acetate resin is then added and the temperature raised to and held at 160° to 180°C. until all the resin is melted. The temperature (and viscosity) can then be adjusted for proper application. The viscosity of this hot melt can be increased or decreased at application temperature by raising or lowering the ratio of polyvinyl acetate to plasticizer and fluxing agent. In addition, the choice of viscosity grade (molecular weight) of polyvinyl acetate permits adjustment of application viscosity.

Frozen food containers, beer cartons and canned goods cases are coated to increase the strength (increased water-resistance) of the container as well as for decorative purposes. H-B5 is a starting hot melt coating for packaging cartons. Hoechst Wax and Santicizer 160 are melted at 100° to 120°C. Polyvinyl acetate is added and the temperature raised to and held at 150°C. until a uniform melt is obtained.

H-B7 is an example of a hot melt that can be applied at low temperatures, 110° to 120°C. Dibutyl phthalate, Aroclor 1254 and Resin 861 are melted at 120°C. Polyvinyl acetate copolymer resin is added and the temperature held at 160°C. until a uniform melt is obtained. The temperature is lowered to 110° to 120°C. for application.

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The bookbinding industry is an important outlet for hot melt adhesives that are based on alkali-soluble copolymers of vinyl acetate and monomers containing carboxyl groups. H-C1 is a basic formulation for use

where recovery of scrap paper or "broke" is important. The operating temperature of the hot melt will affect the alkali-redispersibility of the resin, so it is necessary to use the more alkali-redispersible grades at higher operating temperatures. In H-C1, Rosin WW may be used as the fluxing resin if lighter color is desired; Nevillac Soft gives lower melt viscosity. Sodium benzoate improves heat stability, while Acrawax C reduces blocking.

Quick-tack to polyvinyl chloride coated paper, water resistance at 200°F. and non-toxicity are some of the requirements of a hot melt adhesiv for coffee cup seams. H-E1 is a typical hot melt starting formulation for this application.

H-B3 is an example of a hot melt adhesive having permanent tack. These latter formulations are prepared similarly to the description given for H-E11. The final melt temperatures and viscosities are indicated in Table I.

Talbe II gives hot melt formulations based on polyvinyl butyral for a variety of applications. The polyvinyl butyral hot melts are prepared in the same manner as those containing polyvinyl acetate except that the final melt is prepared at 30° to 50°C. higher than the application temperature indicated in Table II.

The decision to use polyvinyl acetate, polyvinyl butyral or some other resin as the basic resin component of a hot melt adhesive depends largely upon the specific adhesion of the resin to the surface in questio H-E5 is a basic starting formulation containing polyvinyl butyral resin.

The time-tested and widely used hot melts based on wax, asphalt and natural resins are being challenged by hot melts based on synthetic resins. The latter have increased enormously the variety of applications for which hot melts can be used. Polyvinyl acetate resins and their modifications are prime examples of the kind of resin eminently suited to modern hot melt technology. Film-forming ability, inherently adhesive nature, relatively low melt temperatures, heat and light stability, film clarity and absence of taste and toxic or hazardous handling problem make polyvinyl acetate a basic component of modern hot melt formulations.

Table I -- Hot Melts Containing Polyvinyl Acetate Resins

Designation:	H-E11	H-B5	H-E9	H-B7	H-C1	H-E1	H-B3
Use:	Basic Hot Melt	Protective Coating Paper	Paper Board Adhesive	Low Melting Hot Melt	Alkali Dispersible Adhesive	Coffee Cup Seams	Mylar to Paper Adhesives
Material							
Gelva V-1½							1
Gelva V-7		80	50			60	1
Gelva V-15	46		50				
Gelva--C-3 V-10							
Gelva--C-5 V-16					38		
Resin 861				25			
Nevillac Soft					28.3		
Nevillac Hard	24					10	
Ethocel N-4							
Pentalyn A			100				
DBP	28		33	13	7		
Aroclor 1254				12	27		
Santicizer 8							1
Santicizer B-16						20	
Santicizer 160		20					
Hoechst Wax		20					
Acrawax C	2				1		
Sodium Benzoate					0.76		
Properties:	3000 cps. at 170°C. Non-blocking.	1000 cps. at 150°C. Flexible. Non-Blocking Heat sealable.	3000 cps. at 170°C. Non-blocking.	2000 cps. at 120°C. Non-blocking.	3500 cps. at 175°C. Non-blocking	2500 cps. 1000 c at 170°C. at 150 Quick tack to PVC Permanent coated tacky paperboard	
RMC:	35¢/lb.	44½¢/lb.	29¢/lb.	34¢/lb.	35¢/lb.	52½¢/lb.	39½¢/l

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Table II -- Hot Melts Containing Polyvinyl Butyral Resins

signation:	H-E7	H-G1	H-B6	H-E5	H-E2	H-E3	H-E4
Use:	Heat Seal Label Adhesive	Leather Adhesive	Low Melting Hot Melt	Hot Pickup Adhesive	Wax Paper Adhesive	Frozen Food Container Adhesive	Frozen Food Container Adhesive
Material							
Butvar B-76		20		10	15	18	10
Butvar B-90	10		15				
Resin 861	24		43	74.4	43	25	45
Rosin WW		60					
Ethocel N-10							3
Castorwax	24	25	36	8.3	36	44	35
Armid HT	0.5	0.5	0.7	0.2	0.72	0.9	0.7
Santicizer B-16	6		3	10	4		
Dibutyl Sebacate	2						
Acrawax C					2		
TiO_2 (RA-50)						1.9	
Al-Silate W						10.4	
Properties:	1500 cps. at 150°C.	2000 cps. at 150°C.	2000 cps. at 120°C. Light colored. Slight blocking.	1000 cps. at 120°C. Quick set.	1500 cps. at 150°C.	2000 cps. at 150°C.	2000 cps. at 150°C. Non-tacky Light colored Tough.
RMC:	36½¢/lb.	27¢/lb.	42½¢/lb.	22½¢/lb.	25¢/lb.	35¢/lb.	30¢/lb.

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