Chemical Purchasing 9/75

ADHESIVES

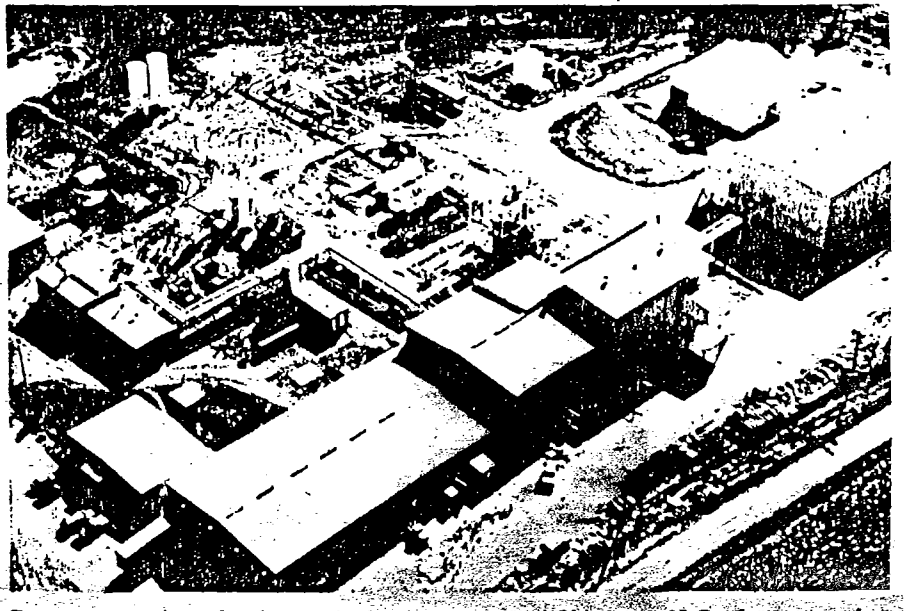
The technologic revolution in the means and methods for fastening materials together will provide for a 10-billion-pound-per-year business during the coming decade.

Adhesives are one of the fastest growing segments of the chemical process industries. This growth will continue to accelerate as the trade responds to new opportunities in industries such as packaging, construction and textiles. There is scarcely an item of everyday life that is not touched in some manner by adhesives technology. From the books we read to the shoes we wear, the role of adhesives is widely accepted but often only narrowly understood in terms of technologic change and development.

Over the past few decades, the adhesives industry has evolved from the use of a handful of relatively simple natural products, including animal and fish glue, casein, starch and natural rubber latex, to an ever-increasing host of sophisticated synthetic materials designed to provide specialized and exacting bonding performance. The technologic revolution in fastening materials together faster, stronger and more economically, will bring new applications for adhesives and sealants in automotive, aircraft, electronics, metal working, and other so-called high performance industries. In many end-use areas, sophisticated adhesives and application systems have already made significant replacements for conventional fastening such as welding, soldering, riveting and nail and screw assembly. It is anticipated that future requirements for adhesives will demand increasingly higher standards of performance governed by more rigorous test methods. In addition, energy, economic, and ecologic considerations will require improved products and application techinques. As a prime example, the use and emission of solvents in adhesive technology will be further curtailed.

Solvent-thinned and carried adhesives have dominated the market for many years. However, they are meeting increasing resistance from pollution, safety and economic standpoints. The trend is toward water-based, hot-melt and other solventless systems. As in the paint business, there has until now often been more talk than action in converting adhesive systems away from solvents. Action, however, is today's byword in formulating solvent-free adhesive products and this trend will increase widely. To accomplish these economic, ecologic and performance changes, new products are being developed to provide specific bonding and sealing functions. Methods of application will in many instances change dramatically to accommodate new adhesive systems and different substrates.

In recent years, because of more stringent performance requirements and new applications, the development of adhesives has become more a science than an art; the adhesives industry has gained its own place in the technical sun. Specialized research in polymers, resins and other raw materials is now devoted exclusively to adhesive applications. Twenty or 30 years ago technical self-sufficiency by the adhesives industry was generally not the case—particularly as related to the development of synthetic materials. The adhesives industry was most often a technical stepchild to other industries such as paint and rubber. Products and raw materials were developed principally for these end uses; the adhesive chemist and compounder were forced to use or adapt what was available. As the adhesive business grew, particularly in the use of synthetics, polymers, resins and specialty additives, suppliers to the trade began to tailor-make raw materials and finished adhesive products to suit particular applications. Some



Recent expansion of polymer production center in Charlotte, N.C., has more than doubled capacity. Photo courtesy AMSCO Division, Union Oil Company of California.

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consumers of adhesives began to develop their own technical expertise to satisfy specialized and highly sophisticated end-use requirements.

A new emphasis on technology in the adhesives business has evolved. Keeping up with the technological change, more often than not, will mean the difference between robust health and merely the survival of a company in the adhesive and sealant industry. There is a technical obsolescence occurring in many industries served by adhesive manufacturers. Rapid technical change will create an increasing number of opportunities and a vast new array of problems to be solved. Mounting emphasis on automation will result in the development to new adhesive formulations and equipment for fast, easy application.

Adhesives and sealants are a multi-billion-pound business which may well exceed 10 billion pounds per year during the next decade—based on an average growth of almost 10 per cent per year. It is difficult to pin down adhesive consumption precisely since the industry is highly fragmented, made up of thousands of companies of every size. In addition, as noted, there is a great deal of backward integration among consumers of adhesives.

Because of the economics of scale, raw material position or other factors in addition to the need for specialized technology, consumers have often developed their own formulations and established compounding and manufacturing facilities. Captive adhesive manufacture may currently account for as much as 25 per cent of total American adhesive production. It is difficult to develop any meaningful data on the captive phase of adhesive manufacture. Industry and government statistics do not define adequately the captive segment. Some companies do not even realize that they are in adhesive production. Many firms purchase proprietary materials such as wax, asphalt, starch, basic polymers, etc., and utilize these in adhesive bonding operations. Because the proprietary materials often serve a dual function, they may be considered either coatings, impregnants or adhesives. It is difficult, therefore, to define which portion of total consumption of that material is used exclusively for adhesive bonding operations.

Adhesive is a broad term and includes among others: glue, cement, mucilage and paste. All these terms are often used interchangeably. Generally **an adhesive is any substance able to hold materials together by surface attachment rather than by mechanical means.** The word "adhesive" is used in this report to indicate any substance applied in any form so as to effect a bond between two or more similar or dissimilar substrates.

The elemental function of an adhesive is that of attachment. If the substance performs the physio-chemical function of attachment, it is considered an adhesive. Adhesives cover a wide range of types, including pressure-sensitive materials, sealing compounds and technical coatings which bond by contact. Included are vehicles for bonding fibres and particles of all kinds such as non-woven fabrics, particle board, flock and ground cork. Adhesives facilitate the production of composite units such as laminates, doors, panels, table tops and honeycomb cores. Frequently adhesives act as a sealing agent against moisture, fluids and gas or provide a more corrosion resistant surface. Total strength can be increased with adhesives by obtaining an even distribution of stress even on surfaces with unusal contours or irregularities. Adhesives range from very simple to highly complex compounds applied by either hot or cold processes, with or without pressure.

Wet or dry technique

Generally speaking, adhesive bonding is accomplished through either a wet or dry bonding technique. Wet bonding, simply stated, involves a deposit of liquid adhesive film upon one or both substrates, combining of these substrates, and the application of a pressure or compression cycle to the bonded assembly until such time as the liquid adhesive film has assumed structural proportions. The bonding concept involves the transformation of the liquid adhesive film into a load-bearing continuous film. This transformation may occur simply by the removal of the liquid phase of the adhesive.

A prime requirement of wet bonding is the ability of at least one of the substrates to absorb or transmit the solvent or carrier phase of the adhesive system. Lacking such an ability, the adhesive liquid would remain permanently entrained between impervious substrates and the adhesive would never reach the high solids balance needed to obtain bonding. The removal of the liquid or solvent phase of the adhesive may be accomplished by simply allowing the porous substrates to absorb the liquid, or it may be accelerated by the introduction of heat into the assembly or the passage of absorbing air over the glued assembly. In many packaging applications the latter two absorbing forces are combined in the drying tunnels of a sheet or film laminator. In addition to solvent removal, the wet bonding process often involves variations in the manner in which the fluid adhesive film is converted to a self-supporting film.

Adhesive particle coalescence of the interface can be accelerated or accomplished for certain adhesives by catalytic action. In some systems the catalyst is capable of not only accelerating the cure rate but also of increasing tensile strength through the creation of a crosslinking polymer system with the ability to better withstand the intrusion of oils, solvents and water. In addition to catalysts, some wet adhesive polymer films are cured by dielectric heating, ultraviolet radiation or electron beam. Advance curing techniques are the basis for many newly-developed solventless, wet process adhesive systems. Despite the manner in which it is accomplished, whether by internal chemical reaction or by the simple removal of the solvent phase of the adhesive, the primary requirement of the wet adhesive bonding method lies in the transformation of a liquid adhesive film, possessing neither sufficient strength nor tack to retain the adhered interfaces, into a continuous film of self-supporting dimensions.

Dry adhesive bonding usually refers to that process by which the adhesive is applied in a liquid state to one or both substrates, dried to a relatively tack-free film, and at a later point activated by the application of heat and/or pressure as the adherend surfaces are brought together. Dry bonding is adaptable to the joining of materials which are impervious and will not allow the passage of the solvent phase of the adhesive system. The combining of plastic or metallic films is often accomplished in this manner. The term dry adhesive

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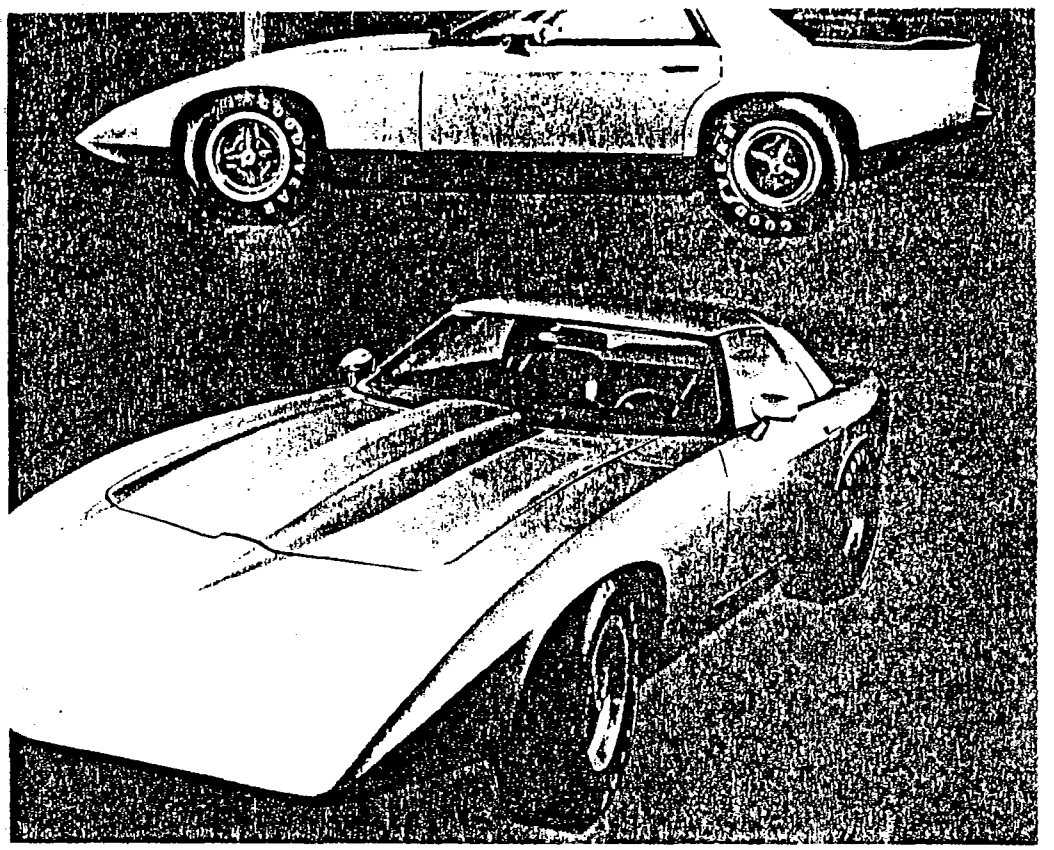
bonding is usually related to the bonding process involving polymeric materials contained in solvent solutions for deposit on impervious substrates and later reactivated under heated nip rolls. The terminology, however, is also applied to adhesive systems, such as natural rubbers, neoprene latices, etc., which display excellent cohesive properties —the so-called contact cements. In contact bonding both adherend surfaces are usually coated.

In the description of adhesive bonding classifications, there are differences in interpretation and overlaps between wet and dry methods. Remoistable adhesives may be classified by some as dry bonding materials, since they are found in the dry state until immediately before activation by water or organic solvent. Others say that these remoistables are more correctly called wet process since the actual bonding occurs while the adhesive film is solublized by the reactivating solvent. Up until now the solvent based or wet process adhesives dominate the market. As the use of solvents declines in adhesives, the so-called dry bonding or solid adhesive forms will take over a larger share of the market—assuming of course that one classifies 100 per cent solids liquid adhesives as dry process. These 100 per cent solids liquid adhesives would of course have to be activated by catalyst, heat, pressure or some outside energy source to form a continous or self-supporting film. While more ecologically acceptable than those adhesives thinned with organic solvents, the so-called water based materials generally fit the category of wet process because the liquid must be removed before a suitable bond can be developed. Water systems by the definition we have chosen cannot be used to bond impervious substrates by the wet process. Water systems have this limitation as well as a much slower evaporation rate than most common organic solvents used in adhesives. This slower evaporation rate of water usually requires energy source and equipment changes to maintain equivalent machine speeds and production rates.

Change is not new to the adhesives business. Over the past few decades, the adhesives product base has shifted steadily from natural materials to synthetic resins. Methods of application have changed dramatically, too. The growing number of synthetic materials, substrates and sophisticated end-use requirements has placed a new emphasis on technology in the industry. Natural products as adhesive raw materials are continually losing their share of the total market in favor of synthetics. In 1970, it is estimated, synthetic resins accounted for slightly more than one-half of adhesive bases. By 1980, approximately three-quarters of the volume will probably be synthetic.



Body structure of Chevrolet's experimental Car XP-898 is completely bonded with vinylester and polyurethane adhesives. Photo courtesy National Starch.

Adhesives are comprised of two types of materials, natural and synthetic. Natural bases can be of animal, plant, mineral or earth origin. Synthetic materials encompass synthetic latices, reacted natural latex, petroleum resins, reclaimed rubber, and thermoplastic and thermosetting synthetic resins. Each basic adhesive material offers certain well-defined advantages which recommend it as an adhesive substance. However, there is no such thing as a universal material. Each material has peculiar limitations as related to adhesive capabilities with different substrates.

This leads to a vast multiplicity of compounded materials often made up of several ingredients to perform specialized functions. As adhesives technology evolved, particularly in the development of synthetic polymers, the trend had been to less blending and compounding to meet performance characteristics. Instead, polymers are now being designed to do almost the entire bonding job with only minor additions of modifying agents. This trend will continue as end-use requirements become more demanding and the chemistry to solve problems becomes more exotic and exacting. Rapid technical change in the industries using adhesives and sealants will create a vast new array of problems to be solved.

The industry

The adhesives industry is composed of relatively few large, well-established full-line producers of industrial, construction, or consumer-oriented products, flanked by a multiplicity of small and medium-sized manufacturers. Many of the smaller producers specialize in a simgle line of adhesives or serve a particular end-use segment of the trade or a geographic area. Relatively little capital investment is required to be a compounder of adhesives; thus the small company can enter the adhesives business and survive if it has the technical and marketing capabilities.

There has been a trend toward merger and acquisition in the adhesive industry over the last several

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years. This has not drastically changed the industry from an overall standpoint. The adhesives industry is still made up of many hundreds of suppliers and continues to be permeated by the spirit of the individualistic entrepreneur. As the technical demands of the industry increase, full-line adhesive suppliers must of necessity be relatively large is size to support in-depth development and research staff facilities as well as national marketing. There is, however, still significant opportunity for specialization in technology by the smaller companies which serve selected end uses, particularly where the companies work closely or jointly with the consumer in solving technical problems. This joint technical development effort is not limited to the smaller companies. As an example, Hughes Aircraft developed high-performance polyimides based on Gulf's proprietary intermediate, benzophenone tetracarboxylic acid dianhydride (BTDA). These polyimides are good adhesives for titanium metal alloys and should have markets in electronics, autos, aerospace, appliances and as solid lubricants. While the basic materials were developed by Hughes Aircraft, Gulf has acquired the exclusive marketing rights.

Industrial users of adhesives have in recent years, developed their own technical staffs. These are primarily concerned with the use of adhesives within their own companies. Their chemists and engineers work closely with adhesive suppliers in product development and problem solving. As might be expected, the purchasing departments of many companies become a focal point for this type of joint effort. The aircraft, textile and graphic arts industries were among the first to develop this approach. The continuing trend toward specialization has produced adhesive specialists who have significantly aided the development of new adhesives both within their own companies and within the adhesive sealant industries in general.

Because of the fragmented nature of the adhesives industry and its early lack of technical expertise and depth, the evolution of moving from a technical art to a science has not been easy. In addition to joint customer/supplier efforts, trade and technical associations have played a significant role in fostering technical expertise.

There is fragmentation among suppliers and consumers of adhesives, but there is no consistent pattern of use of different types of adhesives in a given end-use area. It is next to impossible to establish a meaningful correlation between basic adhesive types and the industry segments that these types serve. Industrial usage by its very nature is such that a single industry may run the gamut of adhesive types ranging from simple vegetable pastes to complex, high-molecular-weight synthetic polymers. A recognition, however, of the basic physical characteristics of each adhesive type permits a projection into the end-use applications of adhesives.

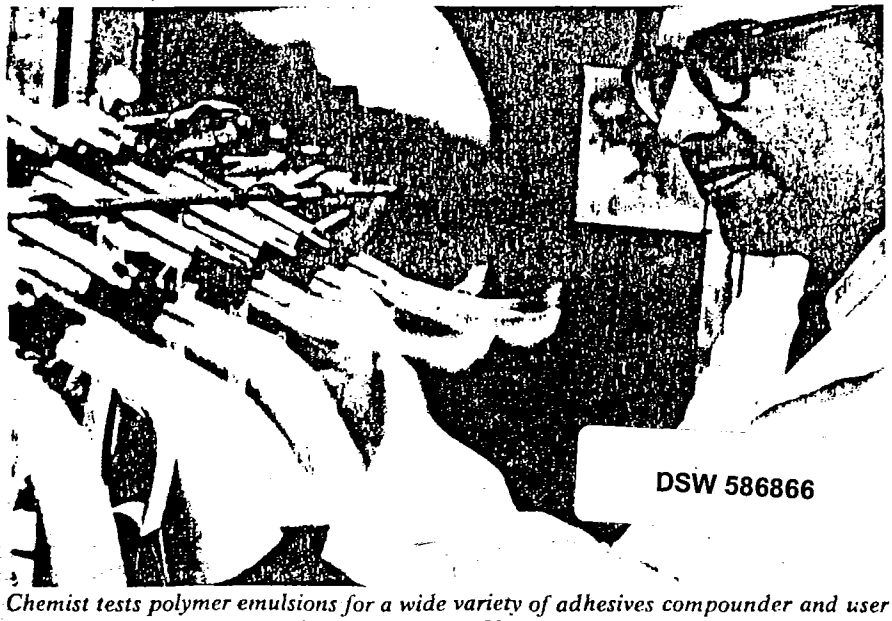
The largest of the markets for adhesives is paper and packaging. Well over one billion pounds of adhesives are presently consumed in this market. A moderate growth of three to four per cent per year is expected for years to come.

The product mix will undergo substantial change, however, as synthetics continue their replacement of natural materials. Paperboard products, both corrugated and laminated, will probably continue as the major consumer of natural products. This is based on limited technical adhesive performance requirements and the assumption that most natural products continue their relative cost advantages over synthetics (of course at the expense of somewhat limited performance). However, factory modernization and capacity expansions to include high speed equipment are expected to accelerate the growth of synthetic materials. As in other adhesive applications, synthetics are often used because of the ease in tailoring basic polymers, usually faster and easier application, and better control during curing. Cost however, is always an important factor in paper and packaging and where economics dictate, natural materials like starch and dextrin will continue to be used.

Adhesive product mix

Despite the inroads of plastics, converted paper products will account for some 40 per cent of all packaging materials for the next several years. The adhesive product mix for converted paper will continue to change as the industry promotes preprinting and high-speed machinery. Hot melt adhesives will gain a further share of this market. Flexible packaging will account for approximately 20 per cent of the market in the years ahead, but there will be changes in adhesive systems. Peelable adhesives will increase for blister packs, unit dose drug packages and meat packaging, both thermoformed and flexible. However, competing materials in flexible packaging, such as heat sealable film, will reduce some adhesive requirements.

For packaging and other applications, adhesive tapes, labels, stamps and decals, all requiring good weatherability, will consume more synthetic adhesives whether they are pressure-sensitive or not. Pressure-sensitive adhesives remain one of the fastest-growing segments of the industry, both in packaging and non-packaging applications. Pressure sensitive adhesives are used



Chemist tests polymer emulsions for a wide variety of adhesives compounder and user applications. Photo courtesy AMSCO Division, Union Oil Company of California.

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among others, in transparent tapes, masking tapes, wood grain panels and racing strips for automobiles, bumper stickers, labels, decorative adhesive backed paper for shelves, cabinets and walls. It is estimated that in the overall pressure-sensitive adhesives, packaging and non-packaging, consume almost 500 million pounds of polymers, elastomers and tackifying resins. The resins utilized cover a broad range of natural and synthetic rubbers, hydorcarbon resins, natural tackifiers, as well as synthetic polymers based on acrylics, vinyl acetate, ethylene and others. To date, the predominance of these pressure-sensitive adhesives, which are applied by the wet process, are based on solvent systems other than water.

Pressed to make changes

Because of the spreading legislation against solvent emissions from adhesives, producers and consumers of pressure sensitives are being pushed to make changes. The high capital cost of equipment becomes one of the major considerations in finding an answer to the solvent emission problem. Existing application equipment for solvent-based adhesives was installed at high cost. The equipment has not yet expended much of its worthwhile or useful capital life. Equipment modifying existing systems to accomplish recovery, recycling or incineration with after-burners is also costly. On the other hand, new non-solvent application is also very expensive. In addition, it requires new techniques and new adhesive polymers, and possibly reduced productivity rates. For economic, technical and performance reasons, therefore, change in solvent-based pressure-sensitive adhesives won't come overnight. However, most new equipment which has been installed over the past few years is capable of non-solvent application.

The technical change to solventless or waterbased systems is not easy. Duplicating the properties of some natural, synthetic-rubber based or compounded materials with years of performance history takes considerble research and testing. Some pressure-sensitive systems such as those based on acrylics are more readily changed. Adhesive engineers already have wide experience with solvent-based [illegible] predict performance with some accuracy when converting acrylics from a solvent system to water based or ultra violet cured.

There are often advantages gained when converting from solvent systems which offset some of the troubles and economic costs. Pressure sensitive acrylics are for example being used on polyester film for clear packaging and tape applications, and replacing rubber-based adhesives coated on cellophane. Polyester film and acrylics have good weatherability and resist UV degradation and discoloration. Both cellophane and rubber have tendencies to discolor and degrade. The technical evolution, as an example, has been a move from solvent-based rubber to solvent-based acrylic with a switch to water-based acrylics, in some instances, now accomplished or in progress. The transition can be more readily accomplished because the performance of acrylics in water systems can be better predicted, based on experience, in solvent systems. In addition, water-based acrylics frequently do not need post compounding or the addition of plasticizers to remain tacky. When used in pressure-sensitive adhesives, natural products, rubbers and solvent-based polymers often require the addition of tackifiers, which may be non-permanent, to obtain the properties of peel adhesion, shear resistance, tack and an overall balance of cohesive and adhesive strength.

With the sophisticated polymer technology of today and the availability of specialized monomers and polymerization aids, adhesive research chemists can now build all desired properties into the water-based resin, eliminating the need for the post addition of modifying agents. In the past, solvent system elastomeric-based pressure-sensitive adhesives might contain as much as 100 parts of tackifying agent for each 100 parts of rubber. The changes in pressure sensitives being brought about by ecologic, energy and economic demands are often reaping side benefits in improved performance and new applications. Masking tapes, using pressure-sensitive adhesives, were principally developed so that automobile manufacturers could paint two-tone cars. As pressure-sensitive adhesive tech-

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in high-performance electrical insulation and temperature work. Newer applications for pressure sensitives other than packaging range from coating both sides of a foam to provide mounting strips for mirrors, pictures and the like, to non-slip rug backing.

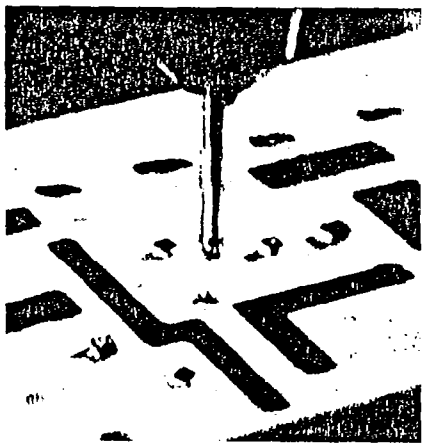
Although hampered by the current economic downturn, the construction industry represents one of the fastest-growing markets for adhesives. Growth is generally on the order of 10 per cent or more per year for adhesives and sealants used in construction. Total consumption of adhesives in construction will probably exceed one billion pounds per year in the early 1980s. Cost is of great importance in selecting materials, including adhesives in the building industry. Therefore large quantities of rubber, tars and asphaltic materials modified with synthetic resins will continue to be used, particularly in the field. However, again mainly because of cost factors, there is a vast opportunity for the use of new adhesives in construction to improve productivity, reduce labor costs, and provide better performance with new building materials such as plastics.

Increased use of prefinished products, the trend toward factory-built homes and modular units provides a tremendous opportunity for structural, laminating and reinforcing adhesives. The bonding of dissimilar plastic to plastic, plastic to metal, glass, stone and concrete requires special resins and adhesion promotors to maintain bond strength over periods of extended use and severe changes in environment. Concrete highway construction and repair is currently utilizing significant quantities of styrene-butadiene latex to bond new concrete to old on interstate highway bridge decks, as well as to provide a barrier and filler for the concrete, impervious to water and de-icing salt penetration. This repair and application technique is used in states where severe winter weather brings about spawling of the concrete by freezing of water in the concrete pores or corrosion of the steel supporting rods and mesh on bridge decks.

This end use for latex is one of many in construction and other industries that illustrate the use of an adhesive to perform additional functions of sealing or reinforcement in addition to bonding. Rather than use hammer and nails in field construction, adhesives and systems are being developed to bond plywood directly to joists in single-layer glued floor systems. This type of system not only reduces labor and material costs but can provide stiffer floors under some conditions. Continued growth in materials such as particleboard and prefabricated wood products (flush doors and plastic laminates) will require increasing quantities of adhesive bonding agents. Phenolics, amino resins, epoxies and other thermosetting types of adhesives are big in plywood, particleboard and prefinishing production.

The use of phenol and urea formaldehyde bonding resins in plywood, particleboard and hardboard manufacture is in itself a billion-pound-per-year business. New engineering approaches and changing utilization of old and new construction materials will bring about other increased utilization of adhesives and sealants in construction. Wherever steel construction is used, there is a need for sealants and caulks. Sealants are also essential in buildings where a lot of glass has been used in construction.

Increasing use of this type of construction opens markets for polyurethane, polysulfide, acrylic, polychloroprene (such as neoprene) and other sealing and bonding materials. There is a vast open area for development in the construction area for structural adhesives. Most of the current generation of synthetic adhesives are good for essentially non-structural applications such as packaging, wood and paper. In construction and structural applications, synthetics are generally limited by special tool requirements, special surface treatment, and properties such as poor heat and impact resistance. Consequently, in on-site construction, it is still necessary to perform such functions as welding and brazing. High-cost, specialized application techniques, and often toxicity, generally limit presently-known adhesive materials largely to factory use. Load-bearing applications require adhesives based on thermosetting resins and alloy types. To go out in the field and do the jobs demanded, polymers of the future will probably require inorganic linkages rather than only organic so that they can withstand high temperatures and other performance demands without decomposition or failure. Until such time as this type of exotic chemistry is perfected, there will be a good deal of welding rod, brazing alloys and sand-blasting equipment employed to give new buildings the durability required. While developments will undoubtedly occur, vast quantities of conventional silicone, rubber, oil-based, latex, etc., caulks will still be used together with time-honored roofing cements, wall and flooring adhesives.



Premixed and frozen two-component epoxy adhesives are used to bond microelectronic components. Photo courtesy National Starch.

Furniture industry effect **DSW 586868**

The furniture industry is undergoing a growth in usage of a variety of plastic materials which are changing adhesive requirements substantially. Although polyvinyl acetate may continue to replace casein and animal glue in wood-to-wood applications, its overall growth in furniture may well be affected by the development of different synthetic adhesives required to bond other plastic surfaces. While the growth of the furniture market should match the high level rate of new household formations predicted for the next several years, the manufacture of conventional wood furniture will decline. Plastic laminates, molded plastics, foams and other synthetic materials will have the most growth in furnishings at the expense of wood.

The textile, apparel, shoe and related industries consume a multitude of types and forms of bonding materials. The continued expansion of nonwoven fabrics and the development of bonded fabrics will provide a healthy growth stimulus for adhesives consumed by the textile industry. Machinery and adhesive systems have been, and will continue to be,

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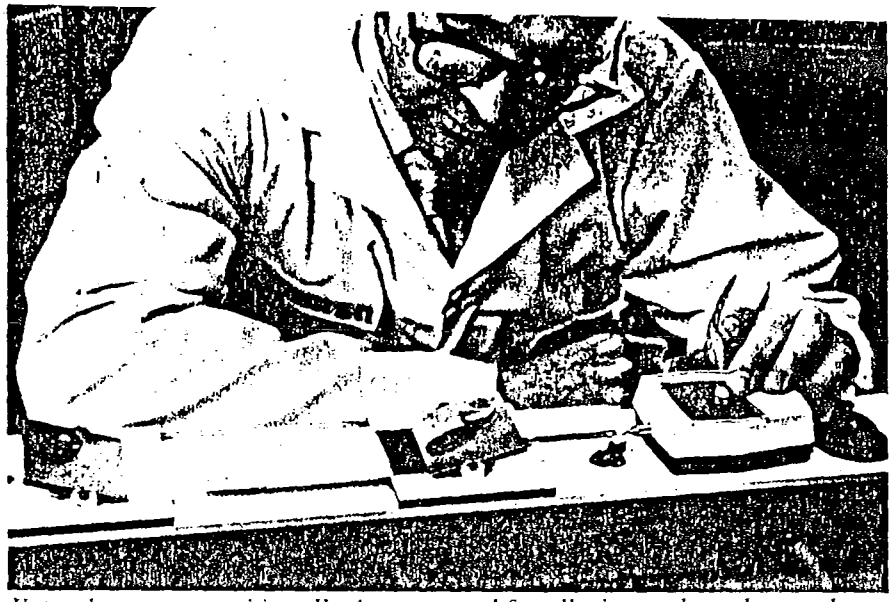
developed to replace many of the conventional stitching operations historically found in the textile industry. On the other hand, in the shoe and footwear business there may well be a decline in the use of adhesives as more and more molded plastic and synthetic footwear is produced. Over the years, adhesive construction had replaced or supplemented stitching operations in the footwear manufacturing business. Now, molding and forming operations are cutting into adhesive demand. Even with molded uppers, or those made of breathable leather substitutes, there is a continuing large demand for adhesives used to attach uppers to soles, which are also made of new plastic materials. Traditional shoe adhesives were of natural rubber, neoprene, nitrile rubber and, more recently, urethane types. As the use of leather uppers and soles decrease, as well as the use of rubber soles, these traditional adhesives have been replaced with a variety of synthetic materials, hot melts, solventless systems, and thermosetting adhesives. Hot melts are available for use in textile and shoe applications affording the required strength without the need for vulcanization required for natural and synthetic rubbers. There are thermoplastic hot melts based on block polymers which flow when heated but set up rapidly. Typical of this type of block polymer are those with end blocks of polystyrene on middle blocks of polyisoprene or polybutadiene. Since hot melts depend on heat dissipation for setting, they bond many impervious surfaces which create barriers for water solvent evaporation.



Hot melt pressure-sensitive adhesives are tested for adhesion, tack, peel strength, etc. Photo courtesy AMSCO Division, Union Oil Company of California.

Changing preferences

Changing style and construction preferences can alter the demand for adhesives markedly. Over the past several years there has been an increasing market for flocked goods in textiles for apparel, upholstery, household furnishings, wall coverings and other decorative applications. Original flock adhesives were often based on paint raw materials such as alkyds. As performance requirements such as washability and resistance to drycleaning solvents became more stringent, other materials were utilized in the manufacture of flock adhesives. Depending adhesive and flock printing raw materials included solution vinyls, vinyl plastisols, solution acrylics and urethanes, among others.

Water-based materials, such as crosslinking acrylic latex, came into wide usage in textile flocking to avoid solvent systems and utilize materials which were more adaptable to textile and fabric mill operations. This, of course, often meant that equipment modifications were needed. The drying and curing of water-based acrylic systems were not always compatible with existing equipment based on solvent or part-solvent/part-water-soluble alkyd resins. Existing electrostatic deposition methods for depositing flock patterns were often found inefficient or inoperable in the presence of water. Polymer suppliers, adhesive compounders, equipment manufacturers and the textile mills worked jointly to solve these problems so that the performance and ecologic advantages of water-base systems could be achieved. Adapting chemical raw materials to ever more exacting and demanding requirements of industries such as textiles, for applications like flocking, is not an easy or inexpensive activity. Technical service costs and specialty compounding charges are unfortunately a necessary evil in the adhesives business, particularly in view of the thousands of different formulations produced for the myriad of end uses. While the technical evolution or revolution in adhesives may bring about a greater degree of standardization, it is doubtful that the technical service requirements or expense will diminish much because of the fragmented nature of consumers and applica-

The transportation industry, principally automotive and aircraft, represent continued growth opportunities for adhesives as material and manufacturing changes occur. The automotive industry has found significant applications in assembling parts by bonding. An example of this is the bonding of brake linings to brake shoes. In transportation products, adhesives can offer many advantages in addition to providing a good bond. These adhesives may act simultaneously as a sealant sound vibration dampener or corrosion inhibitor. Automotive and truck producers are increasingly receptive to the use of new designs and new products incorporating new plastic materials which will require different types of adhesives. High-performance materials requiring delicately-balanced stress performance have necessitated the development of a variety of synthetic products for the aircraft industry. Many of these developments are translatable to metal working, electronic and other industries where high performance is a requirement.

Often, specialty adhesives developed for one end use find a host of applications in other areas. The cyanoacrylate anaerobic adhesives are such an example. These materials are sold for both consumer and industrial applications. They have the unique property of forming a bond on contact with only moderate pressure applied. While they are not universal ashesives, they do have the singular capability of forming strong bonds between many materials without the need for heat or added catalyst. Because of costly manufacturing processes and relatively small volume

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of use, these materials are also very expensive. Therefore, use is generally restricted to specialized applications. Alkyl cyanoacrylate adhesives are used to assemble electronic instruments, bond gasket materials, apply strain gages, repair dentures, antiques and musical instruments. They are also used in such other diverse applications as sealing nuts and bolts. While initially only methyl 2-cyanoacrylate was produced, adhesives are now also made from higher homologs; the ethyl, propyl and butyl esters of cyanoacrylic acid. The materials are one-component, solvent-free liquids in air. Upon moderate contact pressure which excludes air, a solid bond is formed.

The adhesives industry will continue to grow in the years ahead with significant opportunities for new products and new applications. The major growth will occur in adhesives and sealants based on synthetic materials. However, natural products will continue to be used where price/performance dictates.

Raw materials for adhesives

As noted throughout this report, the adhesive product base has shifted steadily from natural materials to synthetic resins over the past few decades. The growing number of synthetic materials, substrates and sophisticated end-use requirements has placed a new emphasis on technology in the industry. It has become a rather complicated business from a raw material standpoint, so much so that in effect it has a language all its own. There is a glossary of adhesive terminology which ranges from adhesion to bite, creep, dope, fatigue, interface, modulus, pot life, tack, webbing. Not only is there a vast terminology but there is a wide realm of raw materials used in the manufacture of adhesives, enough to keep even a CPI purchasing manager confused if only by sheer numbers of raw materials. There are not many chemicals that in some small way at least don't find their way into the manufacture of one of the multiplicity of adhesive products.

Generally, raw materials for adhesives are classified by origin, either of natural or synthetic base. In this report, we shall highlight many of the significant raw materials but will not discuss or review auxiliary materials such as solvents. In the compounding of adhesives, some formulating chemist has probably at some time used, albeit in minute quantities, some of every solvent known to man.

Natural base adhesives may be, as previously noted, derived from animal, plant or mineral origin.

Animal origin include:
Animal glue, fish glue, casein, and blood albumens.

Plant origin include:
Starch, dextrine, natural latex, wood rosins, shellac, gum arabic and oleo resins.

Mineral origin include:
Bitumens, ceramic pastes, lead oxides, sodium and potassium silicates.

Synthetic base adhesives include:
Synthetic latices such as neoprene, styrene butadiene, polysulfide, and butyls.
Reacted natural latices including chlorinated rubber, cyclised rubber, and rubber hydrochloride.
Petroleum and thermoplastic resins, including acrylics, vinyls, ethylene/propylene polymers.
Thermosetting resins such as epoxies, phenolics, ureas, polyesters, resorcinols and silicones.

A brief discussion of some selected raw materials, in alphabetical sequence, should enable the reader to get a better overview of the raw material makeup of adhesives. Understanding some of the physical attributes of each raw material or adhesive type to a degree permits a projection of some of the end uses to which they might be applied.

Acrylic resins used in adhesives are found both in solvent systems or as water emulsions. They are usually thermoplastic polymers containing acrylates, methacrylates or other monomers such as styrene or vinyl acetate. The resins generally have adhesion to glass, metals, paper, textiles and metallic foils and can form very flexible films. Acrylics do not have particularly good heat resistance but perform well at low temperatures. Acrylic modified adhesives are widely-used in pressure-sensitive applications, particularly in newer water-based emulsion types. Multifunctional acrylate monomers are being utilized as adhesion promoters and crosslinking components of reactive adhesive systems such as ultraviolet-cured materials.

Albumen is a simple protein occurring in eggs, milk, animal blood, etc. Blood albumen adhesive was previously used in plywood but has been replace by phenolics and ureas. It is still used in moderate amounts in the wood business because of good water resistance and high-shear bond strengths on cellulosic substrates.

Alkyds similar to those used in paints have been used to modify rubber and phenolic adhesives, but, like other solvent base materials, usage is declining.

Animal Glues are derived from the connective tissue and bone structure of animals and are widely used in the paper, container, bookbinding and furniture industries. They have poor moisture resistance and are subject to

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fungus attack.

Casein is obtained from the acid precipitation or lactic fermentation of skimmed milk. Generally casein is obtained from Australia, New Zealand, Argentina and Brazil and is used for bottle labeling, paper and foil laminating and wood products manufacture. In 1974 the price of casein increased steeply and this hastened replacement by synthetics. One of the prime reasons for using casein in prior years was its low cost.

Chlorinated Rubber is produced from the modification of natural rubber and for use is normally dispersed in esters, ketones or hydrogenated petroleum solvents. They have good adhesion to metal but poor oil and solvent resistance. Therefore, they are often used in combinations.

Dextrine is produced by the partial hydrolysis of starch. It is low cost and therefore finds wide use in paper bonding.

Epoxy adhesives find wide use in the construction industry. The epoxy adhesives are generally two-component systems requiring catalyzation just prior to use. Epoxies have good high temperature resistance and high shear strengths. Epoxy resin glue lines do not release solvents to affect the composition of the substrates being bonded or to pollute the atmosphere. They should therefore experience good future growth.

Gum Arabic is a natural gum derived from the exudations of the acacia trees of Senegal and Sudan. It has greater flexibility than starch-dextrin materials. The use of gum arabic in paper bonding and other applications is declining.

Neoprene adhesives are based on polymers of chloroprene and are widely used alone or compounded with other materials such as casein in laminating, contact cements and in joining rubber to metal for construction purposes. Greater strengths and chemical resistance are obtained through heat treating which creates additional crosslinking of the polymer chain and reinforces the adhesive film. Thermosetting resins like ureas and phenolics are sometimes added to enhance this property.

Phenolic thermosetting resins are widely used both as adhesive-base materials and as modifiers for other adhesive systems. The phenol-formaldehyde, phenol-furfuraldehyde, phenol-epoxy, phenol-polyamide, and phenolic resin fortified synthetic latices provide the major classes of phenolic resin adhesives. These adhesives are used with heat and pressure to provide an irreversible thermosetting adhesive film. One of the principal uses for the phenol-formaldehyde group of resin adhesives is in the wood converting industry, where they are used for the lamination of plywood. The addition of phenol-formaldehyde resin to neoprene and to acrylonitrile-butadiene adhesives increases the resistance of the elastomer to cold flow at accelerated temperatures and tends to produce a more oil- and solvent-resistant adhesive film.

Polyurethanes are a group of thermosetting resins produced by the reaction of diisocyanates with phenols, amines, carboxylic compounds, etc. The reaction products possess free isocyanate groups which aid their adhesive properties. Adhesive bonds formed from polyurethane resins display good heat and oil resistance. Polyurethane adhesives are catalyzed or heat-cured to form relatively shock-resistant adhesive films, used in the bonding of rubbers to metal, metal to metal, metal to plastic laminates, etc.

Polyvinyl Butyral—The condensation of butyraldehyde with polyvinyl alcohol produces polyvinylbutyral. Polyvinylbutyral adhesives display good film clarity and are used in the lamination of glass and other translucent substrates. It has not found wide use as a base adhesive substance but is primarily employed as a modifier for other resin systems.

Polyvinyl Acetate provides the base for a wide range of thermoplastic synthetic resin adhesives. These adhesives are available in powder, emulsion, solvent solutions and hot melt forms. Polyvinyl acetate resins supply a base for a variety of paper and packaging adhesive materials. Polyvinyl resin adhesives have also been used in the wood converting and furniture fabricating industries. Adhesive bonds formed from polyvinyl acetate resin display good oil-resistance but weak water-resistance

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properties.

Polyvinyl Alcohol resins are produced by the hydrolysis of polyvinyl acetate. Polyvinyl alcohol resin adhesives exhibit varying degrees of water sensitivity depending upon the degree of hydrolysis of the polymer under examination. Their use is restricted primarily to paper and packaging applications, although they have found some use in wood laminations and in fabric-bonding applications.

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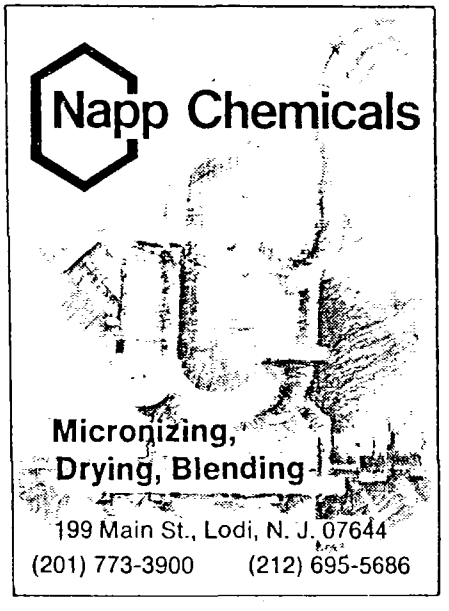

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Resorcinol-Based adhesives are available in liquid resin form or as dry powders. Resorcinol resin adhesives are accepted in structural applications, such as boat manufacture, plywood production, etc., because of their high sheer strengths and excellent resistance to a variety of solvents. Resorcinol adhesives are generally high in cost.

Styrene Butadiene Rubber (SBR) adhesives provide a broad class of synthetic rubber adhesives used by American industry. These materials give the advantages of relatively low cost with improved physical and chemical properties over their competitor, natural rubber adhesives. Although the styrene-butadiene rubber adhesive does not provide all the chemical resistance properties of the neoprene elastomer, they nevertheless do offer good water resistance and excellent film flexibility. There is so much SBR used for tires that the amount used for adhesives is trivial to SBR producers.

Silicone resin adhesives, available either in fluid, resinous, or elastomeric form, belong to a group of semi-inorganic polymers, formed from the reaction of materials such as dimethyldichlorosilane, methyltrichlorosilane and water. These adhesives are noted for their excellent resistance to water and to high service temperature conditions. They are extremely heat stable and are suitable for use over wide temperature ranges. Silicone resin adhesives have been used in structural applications requiring adhesive flexibility at low-temperature conditions and resistance of the adhesive film to oxidation in ozone atmospheres and in direct contact with aqueous matter.

Starches available from corn, potato, wheat, sago, tapioca, etc., provide the base for a wide variety of packaging and paper converting adhesive systems. The volume of starch consumed for adhesive purposes is very large and centered primarily in the paper converting industry. Starch adhesives offer the consumer a low-cost adhesive system with good initial tack properties and with the versatility possible through the modification of the starch molecule.

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Urea Resin's most important form is

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the urea-formaldehyde class of synthetic thermosetting resins. These condensation polymers are widely-used in the wood converting industries. The plywood industry is one of the major consumers of urea-formaldehyde resin. Adhesive films, formed from urea-formaldehyde resins, are light in color, non-staining, and display good cold water resistance.

Zein is a white protein, derived from a by-product of corn processing operations. Zein is usually suspended in an organic solvent and modified with waxes and tackifiers. It finds limited use as a formulating ingredient for hot melt adhesives.

Market, technical trends

The adhesive business, like many others in the CPI, is heavily dependent on the construction and automotive industries. It has been hard hit by the current downturn. In addition, some of the packaging and graphic arts applications for adhesives fall into the frill category and may continue to suffer from the growing attitude of consumer and industrial austerity.

On the bright side, this austerity may bode well for adhesives as means are sought to perform bonding tasks faster and more economically. The adhesive business represents one of the outstanding challenges and opportunities over the next several years as industry moves ahead to meet the technical revolution being brought about by economic, ecologic and energy conserving pressures. □□

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