

# Factors affecting the selection and performance of silicone release coatings

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The Dow logo is a red diamond shape with the word "DOW" in white, bold, sans-serif capital letters. A small registered trademark symbol (®) is located to the right of the word.

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# About the author

## Darrell Jones

Darrell Jones was the epitome of a Dow Corning “Scientist” – a visionary, a creator, an innovator of release coating technology.

In the early '70s at Dow Corning Europe, Darrell created the industry's first solvent-based platinum-catalyzed release coatings. In the U.S., he had been an important player in the development of solventless silicone release coating technology. He had also advanced more efficient and precise solventless coating methods.

For over 35 years, Darrell had been a key member of the Dow Corning scientific community. What follows is one small “chapter” of Darrell Jones' “book” of silicone release coating technology. For those who knew Darrell, this paper will read like a conversation with a trusted friend.

## Introduction

Release coatings are generally used to prevent things from sticking together! This simplistic statement embraces a wealth of technology and a global industry involving both silicone and nonsilicone materials. At their simplest level, fluids or powders are coated or sprayed onto a surface to provide a nonstick surface for another material subsequently brought into contact with the anti-adherend. This type of release agent is *non-permanent* and usually results in significant transfer of release agent to the released surface. This transfer is called migration or offset. Migratory coatings include soaps, oils, fluorocarbons, silicone oils and even, under the right circumstances, water. They are effective because they form a weak boundary between the two surfaces and result in release agent being lost from the original treated surface, such as a mold, and being transferred to the released surface as surface contamination. We shall not concern ourselves with such release agents here.

A somewhat more sophisticated set of materials is *semi-permanent* release coatings. These result in some transfer to the released surface, but it is a much smaller proportion. The release agent, itself, is not usually a simple fluid but a compounded material involving solid materials dispersed in fluids or oils. Semi-permanent coatings include wax dispersions, mixtures of silicone resins in silicone fluids, micas in various fluids and organic resins such as acrylics.

Temporary and semi-permanent coatings are only mentioned to highlight the specialized nature of our subject, which is essentially nonmigratory coatings that are permanent (or at least capable of multiple uses) and have excellent anti-stick properties. These materials are dominated by silicones, but some organic materials, such as urethanes, fluorocarbons and acrylics, can be used when either toughness of the release surface or absence of silicone is of greater importance than absolute ease of release. In this treatise, we are only concerned with silicone release coatings. Silicones in many forms offer excellent release properties, but to present a nonstick surface and, at the same time, offer little or no transfer to the released surface, we need to form a cured filmic surface free from migratory species. This presents many challenges, and we shall examine various approaches used to meet them.

Polydimethylsiloxanes have several unique properties. Low surface energy from the dimethyl groups and the great flexibility of the siloxane backbone are the two that make the formulation of release coatings possible. Silicones, or polydimethylsiloxanes (PDMS for short), offer a dimethyl surface to the air. This dimethyl surface has a very low surface energy. A convenient measure of this is surface tension; for PDMS, surface tension is 21 to 22 dynes/cm. Low surface energy alone, however, does not guarantee a good release surface. The silicone backbone is an extremely flexible polymer chain with virtually unhindered rotation about all the Si-O-Si bonds. This flexible backbone, together with low surface energy, are the essential elements of silicone's unique release capability. However, even these two properties are inadequate to give a nonmigratory release surface. To achieve that goal, we must find some way to tie all the polymer chains together in a coherent film. This involves the use of crosslinking, or curing, chemistry, which brings us to the crux of this discussion of curable silicone release coatings.

## Release coating markets

As the name implies, release coatings are employed to render surfaces antiadhesive. By far, the biggest single use is to make release liners that carry and protect pressure-sensitive adhesives (PSAs for short) until the moment of use. For this application, the most important substrate is paper. PSA-coated materials include labels, tapes, over-laminating films, sign lettering, medical devices and a host of smaller applications. The release liner's role is to protect the adhesive until it is at the point of application where it must peel away cleanly with little use of force. This basic function is true of all PSA applications whether the liner is discarded, as in a label or decal, or an integral part of the pressure-sensitive product such as a selfwound tape.

Other markets for release liners that are *not* pressure-sensitive adhesive-based include carriers for oily and sticky masses such as sealants, gaskets and mastics; interleaving layers for rubber processing; and support and release base for the casting of plastic films such as polyethylene, polyurethane, acetate and vinyl films. Liners in this last group are often embossed to

impart texture to the cast film. Further examples of release liners include food processing aids such as baking or pan liners; food packaging materials such as gum wrappers; asphalt packaging, in the form of coated drum interiors; release-coated inner-layers of paper sacks; and caul or separating sheets for the production of high-pressure plastic laminates.

One final example of significance is the release liner for tiles and shingles. This application is, in essence, a pressure-sensitive adhesive application but differs from the earlier examples in that one needs a fairly firm bond between the release sheet and the adhesive to prevent premature removal of the liner. This is particularly important as tiles and shingles are stacked for storage, and any exposure of the adhesive leads to the tiles sticking together.

The end uses of these PSA constructions are as varied as the constructions themselves. PSA products are used in the medical, construction, automobile, graphic arts, electrical and electronic industries. Electronic data processing consumes vast quantities of pressure-sensitive labels, most of which turn up in the average household as address labels on bills and advertising material. Supermarkets also use significant quantities of pressure-sensitive labels as price-weight labels, special-offer labels and, increasingly, in the form of a complex label that also includes a discount coupon. Most of today's special mail and package delivery operations use pressure-sensitive bar code labels as check systems to monitor the progress and delivery of packages. Labeling systems are being developed to provide hospitals with permanent records of patient treatment and progress. Most of today's tamper-resistant packaging is based on some form of pressure-sensitive labeling system. The list is endless and grows daily as greater and greater innovation is displayed by the pressure-sensitive industry. Ten to 15 years ago, it was generally concluded that about five percent of the labeling industry was based on pressure-sensitive materials. In 1995, that figure was estimated at 45 to 50 percent.

A similar state of affairs exists in the tape field. The most familiar tapes are office and household tapes based on cellulosic or clear plastic films. These do not normally involve the use of silicone release materials. However, tapes have a very wide range of capabilities and uses. In the packaging field, greater strength in both substrate and adhesive is required, and these more aggressive adhesives do necessitate the use of a release coating. Depending on the adhesive type and the requirements of the application of the tape, this release coating is often silicone based. Electrical insulating tapes, wrapping tapes, thermal insulating tapes and decorative tapes are all areas where silicone release coatings find use.

In the non-pressure-sensitive field, in addition to those applications already given, some newer specialized markets are developing. One of these is for carbonfiber/epoxy laminating materials. Although silicones used in this field have had some problems related to silicone migration, silicone release coatings can be made that perform satisfactorily in this demanding application and provide a stability of release not found with

other materials. Another growing use is an anti-soil treatment for surfaces where water, oil and dirt repellency is required, such as high-quality decorative labels.

In considering these diverse markets and applications, both pressure-sensitive and non-pressure-sensitive, we must also keep in mind that the release coating is usually a very minor part of the construction – approximately 1/2 to 1/4 of a percent by weight. The other components have a very wide range of material choices, also. The release liner, upon which the silicone is coated and cure, can be paper, plastic, plastic-coated paper or metallic. The paper itself can also vary widely, ranging from dense types such as glassine to porous materials such as machinefinished kraft. Clay-coated and other coated papers are also widely used. Plastic substrates include polyethylene of various types, polypropylene, poly-halogenated olefins, polyester and acetate films. Metallic films and paper are also encountered as release liner bases.

Different liner materials have a profound effect on the choice of silicone, both in the nature of the curing chemistry and on the physical form of the coating. Of equal impact is the nature of the adhesive mass to be released.

## **Pressure-sensitive adhesives**

This subject is covered in great detail in many publications, and it is not my intent to delve into it here. However, when one talks of release coatings, one cannot ignore the fact that it is the total construction that is under consideration. In the case of pressure-sensitive adhesive materials, the silicone is about 1/15 to 1/20 the mass and thickness of the adhesive, and it is the adhesive that dominates the performance.

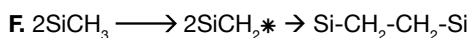
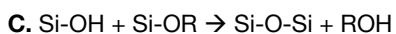
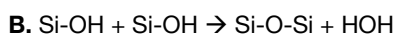
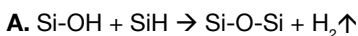
Factors affecting release will be discussed later, but for now, suffice it to say that rheological properties are most critical. These rheological properties are controlled by the chemical nature, molecular weight and formulated composition of the adhesive. Cost and performance requirements influence chemical nature, so acrylic, SBR, natural rubber and other synthetic rubber and epoxy-based materials are common alternative adhesive chemical types. Solvent-based, water-based and 100 percent solids or hot melt are the alternative delivery systems. This has a major influence on the molecular weight of the adhesive materials used. Finally, adhesives are asked to perform under varied conditions such as the normal to high temperatures encountered in shop window displays and the low temperatures to which freezer labels are subjected. Adhesives may be required to be permanent or easily removable without damage to the labeled article. In the tape field, it is often desirable to remove the tape without leaving adhesive behind.

All these adhesive requirements will alter the nature of the total pressure-sensitive construction and, in turn, demand a wide range of release behavior from the silicone. To achieve that range of performance is the challenge before silicone release coating technologists. Consider the means at their disposal:

## Curing chemistry

As stated earlier, in addition to releasing materials in a controlled fashion, a release coating is really only useful in the pressure-sensitive industry if the performance of the released adhesive is unimpaired by silicone transfer. To minimize silicone transfer or migration, the silicone must be tied together in a cured, coherent film covering all the supporting substrate or liner. Maximum release performance is obtained from maximizing the dimethyl content of the cured film. There is the beginning of a conflict that persists in all release-coating formulations, even today. Speed of cure is best served by a high concentration of curing groups and catalysts, whereas release performance is enhanced by a maximum concentration of dimethyl siloxane groups.

The following curing chemistries all had advantages and disadvantages.



**Example A:** The advantages of this chemistry are that it is very fast when a suitable catalyst is used. It is also inexpensive and easily made into polymers. This chemistry is not susceptible to poisoning, so it is unaffected by potential substrate inhibition. The disadvantages include great difficulty in putting the SiOH anywhere except on the terminal silicon atoms of polymers. This system needs a catalyst, normally an organotin salt. Because it is not easily poisoned, it is very difficult to control bath or working life once catalyzed. Hydrogen evolution can be a problem under certain circumstances.

**Example B:** This is the condensation reaction and clearly could also occur in Example A. It is a fast reaction, but when the silanol groups are only on the terminal groups of polymers, it is not as fast as Example A. Because it is difficult to build a polysilanol-functional molecule, it is difficult to crosslink a curing film, and this reaction, on its own, is not a good basis to make cured films. The use of organotin salts accelerates the curing, but the basic reaction is reversible. This is not desirable because of the potential to create migratable species.

**Example C:** This chemistry has several advantages. Polyfunctional -OR molecules are easily made as tetra-, tri- and di-alkoxy silanes. A wide variety of alkoxy and acyloxy groups is available. Within this range, cure speed varies from very fast to very slow. Unfortunately, the more common alkoxy groups, such as methoxy, ethoxy, etc., are slow curing. More complicated groups, such as aminoethoxy or alkoxy groups containing either linkages, are very fast but are also very hydrolytically unstable, making them somewhat unstable, making them somewhat unsuitable as groups for polymeric molecules. However, when used with silanol-terminated polymers,

these alkoxy groups can form excellent crosslinking materials either as oligomers or silanes. The chemistry benefits from the use of a catalyst, but it is difficult to control the bath life.

When the -OR group is an acyloxy group, catalysts are not necessary; but the liberated acid, such as acetic acid from acetoxy group functionality, is a definite problem in terms of its effect on the substrate and machinery and its volatility and effect on adhesive mass.

**Example D:** This is a variation on Example C and uses moisture as a reactant. This chemistry is the basis of some sealant technologies and can be used in release coatings, especially when used with a titanate catalyst. However, bath life and cure speed are not good, and this option has been widely used.

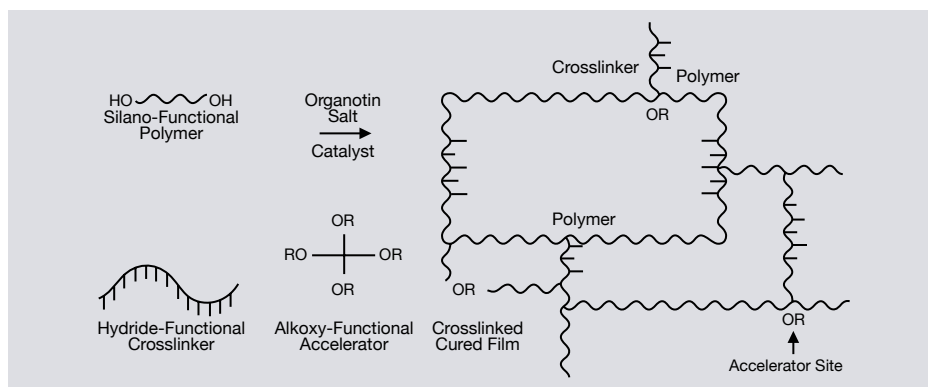
**Example E:** This chemistry is very different from the foregoing examples. This system needs a catalyst, normally an organoplatinum complex. With this catalyst, the system is easily poisoned or inhibited. This is a clear disadvantage when the substrate inhibits cure, but when inhibition is used in a controlled manner, a long working bath life can be obtained. This is especially advantageous when considering high solids or even 100 percent solids materials.

**Example F:** Normal polydimethylsiloxanes can be cured into rubber-like materials through the use of peroxide curing agents. In theory, this is a very desirable system with the maximum amount of dimethyl siloxane. In practice, several difficulties prove overwhelming. First, this kind of chemistry is inhibited by oxygen. Release coatings are virtually all surface, the film being only about 1 micron thick, so surface effects such as oxygen inhibition have a dominating effect. Second, to ensure no free polymer content, which would lead to migration or silicone transfer, a high loading of peroxide is necessary. This leaves a contaminant with no release properties in the cured film, offsetting the gain in dimethyl content. Finally, the curing temperature for such peroxide systems is quite high and damages the substrates, especially heat sensitive materials. Although this chemistry is widely used in the silicone elastomer industry, it is not used for release coatings.

This list is not exhaustive but does cover the most obvious alternatives facing the release coating technologist. In the early days of the technology, Example A was the chosen technology. Polymers were made with silanol end groups, and crosslinkers were made from poly-SiH-functional oligomers. Catalysts such as dibutyl tin di-2-ethylhexanoate were used at levels of 2 to 15 percent by weight.

In later years, the chemistries in Examples C and D were employed to accelerate the cure rate of Example A. Both siloxane oligomers and silanes were made with very reactive alkoxy ligands. These reacted with both silanol from the polymer and water from the atmosphere and from the paper to produce polysilanols, which are very reactive and accelerate the cure substantially.

**Figure 1.** System schematic.



The schematic for this system is shown in Figure 1.

Control of release performance, which will be discussed in more detail later, involves controlling the elasticity, or crosslink density, of the cured silicone film. With this chemistry, this is easily achieved by controlling the chain length of the polymer. Polymers ranging from 20 to 5000 siloxane units, were employed. Because of the difficulty of controlling this set of reactions, working bath life could only be achieved by working in dilute dispersions, either as solutions in solvents or as oil-in-water emulsions. One hundred percent solids operations were virtually impossible with this chemistry, which comprises the so-called condensation or tin-catalyzed system still widely used today.

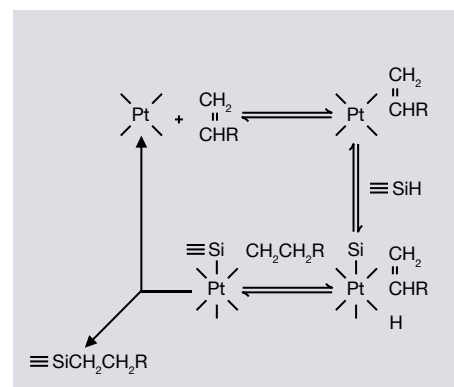
The advantages are fast, low-temperature curing, relatively wide range of release available through polymer molecular weight control, and freedom from substrate inhibition. The disadvantages are somewhat lengthier. There is no 100 percent solids alternative; indeed, even in solvent it is difficult to operate much above 8 percent solids. The reversible nature of Example B chemistry leads to a phenomenon called blocking in which liner coated with silicone on both sides tends to bond to itself on storage. The tin catalysts are used at quite high loadings and can alter the adhesive behavior on aging. Migration tends to be more prevalent with this chemistry.

These coatings were the basis of the silicone release liner business from the late 1950s until the mid 1970s. At that time, the environmental pressure on solvent emissions made the development of 100 percent solids coatings a paramount need.

To meet this need, the addition-curing chemistry shown in Example E became the preference. The addition of a silicon hydride group across a vinyl group is catalyzed by a few parts per million of platinum metal in the form of an organo or organo-silicon platinum complex. This contrasts sharply with the 2 to 15 percent of organotin salt used in the condensation system. Being an addition reaction, this reaction has no leaving groups, so nothing is evolved during curing. The curing mechanism is shown schematically in Figure 2.

The presence of another group that can either compete with or exclude the vinyl from the platinum is called inhibition in the first case, and poisoning in the second. The difference is purely one of degree and desirability. In the presence of the catalyst, the addition goes very rapidly with the evolution of heat. In dilute solution, the bath life can be controlled much as in the condensation system, but for high solids or 100 percent solids, selective inhibition must be used.

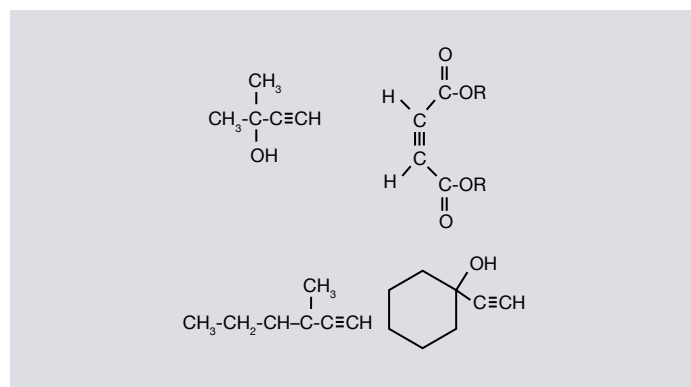
**Figure 2.** Addition-curing mechanism.



Commonly used inhibitors effectively exclude the vinyl groups from the platinum at temperatures around room temperature. At elevated temperatures above 80°C for example, these inhibitors either evaporate or react with the SiH and become part of the cured matrix. In either case, they can no longer exclude the polymer vinyl groups, and cure takes place rapidly. Such inhibitors include various acetylenic alcohols, materials containing conjugated double and triple carbon-carbon bonds, various unsaturated dicarboxylic acid esters and some ketoximes. (See Figure 3). Materials such as amines, sulphides, phosphides and the organotin salts used as catalysts in the condensation system from somewhat stronger bonds with the platinum and are generally regarded as poisons. Their presence makes it difficult, if not impossible, to cure an addition-curing coating.

A further highly advantageous feature of this chemistry is the ease of polymer manufacture. While silanol groups are only easily placed terminally, vinyl groups may be placed not only terminally but anywhere along the polymer chain, virtually at will. Furthermore, these polymers will stand heat treatment better than silanol-functional polymers and so are more easily devolatilized. This further aids the cause of migration-free coatings.

**Figure 3.** Inhibitor examples.



Thus, in addition to the ability to control the elasticity of the cured film by polymer chain length is the scope to do so by manipulating both the number and distribution of vinyl groups along the chain.

This chemistry has no reversible reactions in the mechanism and so is free from the blocking phenomenon discussed earlier. There are two major disadvantages. One is the sensitivity to poisoning either by the substrate being coated or by the introduction of

foreign material prior to coating. The second is the inherent cost. Both the catalyst and the vinyl moiety are more expensive than the corresponding condensation-based materials.

The rapid rise in 100 percent solids operations over the past 15 years has meant that economics of scale have offset some of the inherent cost penalties, and a general increase in awareness of the nature of substrate inhibition has rendered much of the sensitivity a minor concern. In the years since the mid-1980s, the addition-cured materials have taken an increasingly bigger share of the market from the older condensation materials. In 1990, the share was greater than 65 percent on a global basis. The use of condensation systems continues to decline.

Although these two systems have dominated the chemistry of silicone release coatings, all the examples given and some others can serve to meet the basic need, which is to form a cured film of silicone in which little or no loose, migratory or extractable material remains after curing. The curing mechanism is necessary to do just that and has no other value. Should a way be found to make a thermoplastic release coating, for example, this curing mechanism would no longer be necessary. Later, under "Future Developments," radiation curing will be discussed. This, too, is but a means to an end. In the release coating industry, the failure of the silicone to completely cure has been the cause of significant problems. At present, however, the cure mechanism of a release coating is perceived to be at least as important as any other property of the system.

## Coating systems

In the early days of silicone release coatings, specialty applications were the norm, and raw material costs were not an overriding concern. As everyday uses became more and more common, cost control became more pressing. Although the silicone is only about 1/2 to 3/4 percent of the weight of the construction, it can be 2 to 6 percent of the cost of a plain pressure-sensitive label and as much as 30 percent of the cost of some silicone liners. Therefore, the desirability of using as little silicone as possible is certainly understandable. The minimum amount necessary will vary from substrate to substrate. Plastic films, with their perfect hold-out and smooth surface, need only about 0.1 to 0.2 grams per square meter (gsm) to effect perfect film coverage and exhibit good release properties. A parchment, on the other hand, may almost unavoidably require 5 gsm as the silicone fills up the surface imperfections. European glassines typically need about 0.7 gsm, whereas North American super-calendered kraft needs a little more, about 1 to 1.2 gsm, for complete coverage.

A coating of 1 gsm is almost exactly 1 micron (one millionth of a meter) thick. The task of applying such a thin coating uniformly and consistently has been quite a challenge to coating equipment manufacturers.

Coating methods can be classified in many ways. One rough division is into methods that apply an excess and then meter off to the required amount, and methods that deliver a precisely controlled amount directly onto the substrate. Examples of the first method are Mayer rods, air knives and blade-over-roll coaters. The best known example of the second is gravure.

In the early days of siliconizing, when only silicone solvent dispersions or water-based emulsions were available, all of these methods were employed. In general, even then, slot-die extrusion, foam coating and spray coating were not successful for a variety of reasons, but predominantly because of the low required coat weight.

Of the accepted methods, direct gravure is the most accurate and the most successful, but Mayer rods and air knives have been used quite widely, especially where slightly higher coat weights are acceptable. All three methods offer two opportunities to control coat weight. The first is the equipment itself – gravure cell size, Mayer rod number, and air knife pressure and impact angle, all of which have a major effect on deposited coating weight. A second opportunity is in the solids content of the coating formulation. With water-based emulsions, it is possible to coat at solids contents of up to 50 percent. However, if the goal is to achieve a dry coat weight of about 1 gsm, this puts a severe limit on the choice of equipment. Condensation chemistry limits solvent-based coating to something under 10 percent solids; and at this low concentration, a wide range of Mayer rods and gravures is available to adjust the final dry film coat weight to exactly the desired amount.

Figure 4. Typical pan-fed, three-roll differential offset gravure.

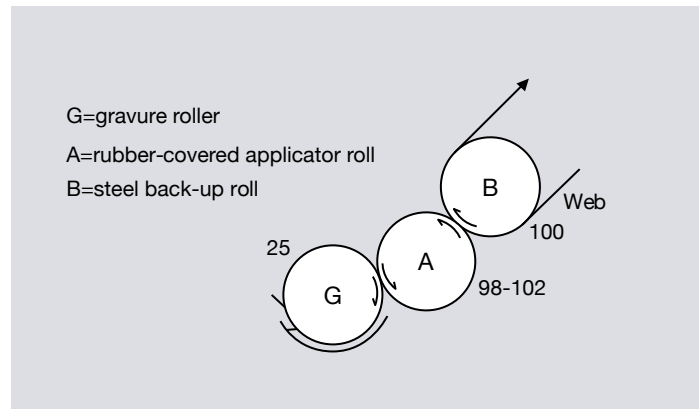
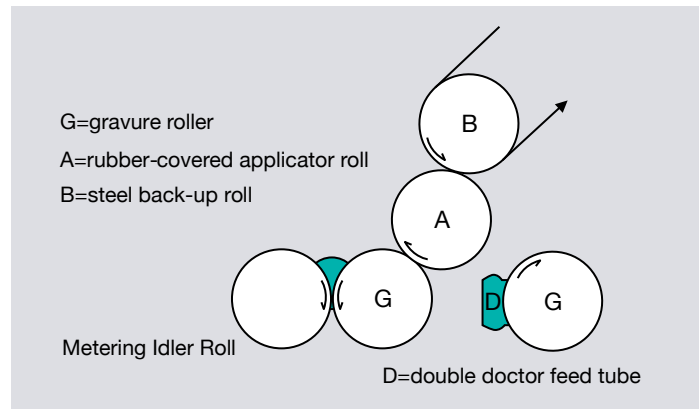


Figure 5. Alternative Feed System.



Coat weights as low as 0.1 gsm and as high as 3 gsm have all been achieved easily with direct gravure and coating formulations ranging from 1 to 20 percent solids – the latter more with addition-curing materials than with condensation types. Very low coat weights are a little more difficult to achieve with Mayer rods.

Both Mayer rods and gravures do have some needs of their own. Neither the gap between wires on the rod nor the bottom of the cells of a gravure empty completely. None of these solvent-based silicones have an infinite bath life, so slowly and inevitably the cells and gaps between wires become plugged with gelled silicone, reducing the volume that can be delivered effectively. Hence, both kinds of equipment need regular cleaning to remove gelled silicone. Monitoring either coat weight or coverage (dye check) can give a good indication of equipment cleanliness. Coat weight measurement and coverage assessment will be covered later under "Testing."

The advantage of the air knife is that no moving parts touch the substrate, so cleanliness is not a problem. This method is not very satisfactory for solvent-based coatings due to solvent loss and viscosity control difficulties, but it works very well with water-based silicone emulsions where the use of viscosity-control agents is relatively straightforward. The coating of diluted coatings by the describing methods is so well established that it does not merit further discussion. Coating with 100 percent silicone solids, however, is a much more demanding affair.

Although achieving 1 gsm coverage is easy out of a dispersing medium such as solvent, it is more difficult at 100 percent solids. A gram of silicone is a ball or drop about 5 or 6 mm in diameter. Spreading this out over a square meter is a significant challenge and will not be achieved with a brush or finger. Whereas the same material dispersed in 20 grams of solvent easily spreads all over, and the 19 grams of solvent is allowed to evaporate. Both the flow-out characteristics and the accuracy of coating become more demanding without the solvent.

The two most common methods used today to apply 100 percent solids coatings are three- or four-roll differential offset gravure and the multi-roll smooth roll coater.

The most demanding aspect of the offset gravure (OSG) system is the balance of the cell size of the gravure and the speed of differential between the gravure and the applicator or offset roll.

Figure 4 illustrates a typical pan-fed, three-roll differential OSG. Not all nips are film-splitting nips. This is not always necessarily so, but it is the most usual configuration. Typically, this setup would use a gravure with 180 to 220 cells per inch of either a quadrangular type or the connected quad (CQH) type; other types, such as helical or pyramidal, are also used. With such a cell size, the applicator roll may turn at 3 to 5 times the speed of the gravure. The web speed would then be within 5 percent of the applicator.

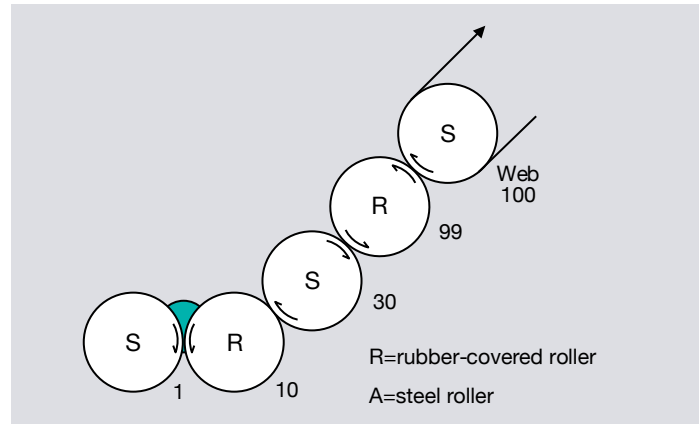
Such a gravure is very fine, easily damaged and plugs quite frequently. The temptation is to use a much coarser gravure of 100 to 120 cells per inch. However, this will necessitate an applicator roll-to-gravure roll differential that is maybe ten times faster. This will produce a poorer silicone film and a less satisfactory coating and, in addition, will put a lot of shear strain on the silicone, which will shorten bath life.

Variations on this system include nip-fed, double doctor feed tube-fed, reverse applicator, and variations in both gravure material and doctor blade angle and material.

In many instances, chrome-plated gravure rollers have given way to laser-etched ceramic-coated rollers. The doctor blade

for the gravure, shown in a negative angle in Figure 4, can be a conventional trailing doctor blade if the mounting is sufficiently strong to resist hydraulic ramping effects on the blade at higher speeds. An alternative feed system is shown in Figure 5.

**Figure 6.** Five-roll coater with typical speeds.



The double doctor blade feed tube system enjoys the same advantage as the nip feed. That is, less coating is needed to prime the equipment than with a pan-fed system. However, both are prone to air entrapment problems, which can be eased by suitable silicone viscosity selection, by careful equipment design and by speed of running.

By and large, the offset gravure has been the method of choice in the USA. In Europe, the multi-roll smooth roll coater has enjoyed more widespread acceptance. This is shown in Figure 6. Note that this is a nip-fed system, and all nips are film splits. The rollers alternate rubber/steel throughout. Typical speed settings are shown, but many variations will work well. In general, speed differentials between contacting rollers are best kept to less than four to one.

Both methods have their advantages and disadvantages. The OSG is cheaper, simpler and does all that is expected of it. The multi-roll coater will achieve a lower coat weight with better coverage and has no gravure to plug up, but it is complicated and needs time to be optimized in terms of nip pressures and roller differentials. It also costs more.

Both methods have a tendency to be speed dependent; that is, coat weight changes as machine speed is altered. Both are susceptible to hardening of the rubber roller as silicone swells the rubber rolls and then cures in the roller. Silicones with "infinite" bath life – electron beam-curing silicones, for instance – do not do this to the rubber rollers.

Both methods work best if the applicator roll is cut to suit the web width, but this necessitates a quick-change system for applicator rolls and further added expense. The debate over the merits of these two systems has continued for several years. If the minimum coat weight expected from the equipment is achievable by OSG, then both will do a satisfactory job. There are other solventless silicone coating heads, but none have gained the acceptance of the OSG or multi-roll coaters.

To sum up, for dispersion coatings (either solvent- or emulsion-based), several well-established methods exist that will achieve any desired coat weight with good coverage on just about

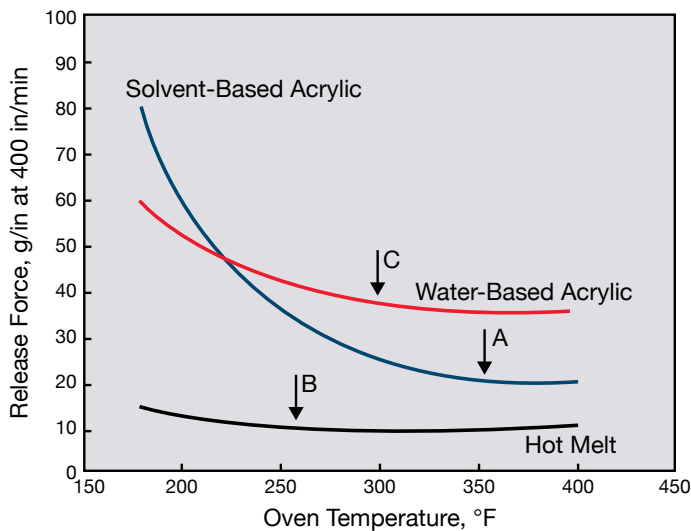
any usable substrate. For 100 percent solids or solventless silicone coating, there are two main methods from which to choose, neither of which will get down to very low coat weight with good coverage. Since filmic substrates need very little silicone, 100 percent solids coating of these substrates is less economical than desirable. There is still an unmet need to achieve 0.2 gsm with excellent film continuity on, for example, polyolefin films.

### The curing stage

Thermal curing only will be considered in this section; ultraviolet and electron-beam radiation curing will be discussed under "Future Developments." Silicone release coatings can be coated out of solvent, water, or 100 percent solids. Immediately thereafter, they all need to be cured by application of heat. Although microwaves will evaporate water and infrared will dry off solvent, the most prevalent method, by far, for curing silicone release coatings is hot forced air. Oven designs come in many forms. Some common types include arch dryers, which help enormously with web tension control; and air flotation ovens, which avoid contact of the web with the oven rollers. These ovens apply heat from both sides of the web and are very efficient heaters. Most new ovens are air flotation types, but some arch or straight-through ovens with only top-side heating have been built. This latter type is an attempt to control moisture loss from cellulosic (paper) substrates.

For dispersion silicones, there are different curing requirements for emulsions and solvents, and both are different from solventless requirements.

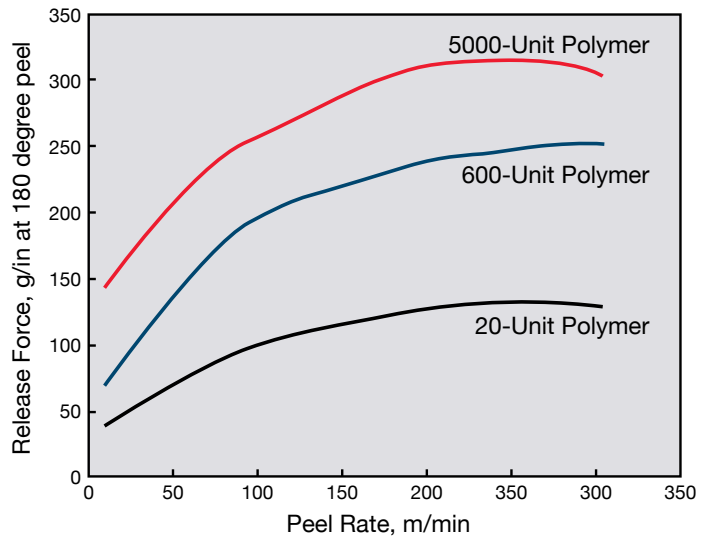
**Figure 7.** Effect of curing temperature on release values.



Consider emulsion drying and curing. As will be discussed in the section on "Formulating Release Coatings," emulsions often contain water-soluble organic extenders or thickeners as well as silicone release material. Thus, the sequence of events is as follows. First, the uniform, wet film of coating enters the oven, and water begins to evaporate. The silicone emulsion particles begin to coalesce, and the thickener raises the viscosity of the film as water leaves. The silicone must coalesce to an oil and move to the surface before it either begins to gel or is prevented from moving by the filmforming of the organic. Second, when

the silicone oil has formed a silicone-rich surface, the rest of the water must evaporate. Finally, the silicone must cure. If the silicone cures too quickly on the surface (and if the organic material forms a surface film also), water will be trapped under the film and will explode holes in it later as added heat forces the water to volatilize.

**Figure 8.** Effect of molecular weight on release force.



If too much heat is applied too soon, not only is the above phenomenon encouraged, but the stratification of the organic and silicone is hindered, resulting in too much organic in the surface and impaired release properties.

Thus is the case for zoned oven heating made. Relatively gentle heat is applied at first to remove the water slowly and raise temperatures to coalesce the silicone. Next, somewhat hotter temperatures are used to remove the last of the water and enhance silicone mobility. Finally, high temperatures are applied to cure the silicone well and harden the organic.

For solvent-based coatings, the scenario is a little simpler. All that is needed is to remove solvent and, in some cases, volatile components such as catalysts, crosslinkers or additives before they become trapped beneath the surface skin. Again, somewhat less aggressive heating in the first part of the oven will remove solvent and begin curing. Too much heat too quickly can cause a race between curing and catalyst evaporation, for example. With condensation systems, it is quite easy to evaporate the tin salt catalyst too prematurely, leading to tin oxide deposits in cooler parts of the oven.

For solventless silicone, the situation is a little different. With 100 percent solids, the uniformity of the coating as it leaves the coating head is often poor – a result of film-splitting effects. Unlike solvent coating, the viscosity of the coating may be over 300 cp, so it needs time to level out. This leveling is accelerated by temperature, but only if curing is not triggered. Also, the crosslinkers can be evaporated by too much heat too early. So, again, the best situation is a zoned, ramped oven, cooler at the front.

In reality, ovens range from 15 to over 300 feet and from single-zone to six or eight zones. Speeds range from 50 to 2000 feet per minute. These conflicting circumstances mean much curing is far from optimum. It is not possible to give curing



requirements in a table form. For a given formulation, the time and temperature required to achieve a nonmigratory, nonsmear, well-anchored film can be defined, but they will be absolutely individual to each oven.

Clearly, when a coating is still oily or smeary and transfers to the adhesive or the backside of the substrate when it is wound up, it is not cured well enough. However, even the best-cured and aged coating may be put against an adhesive and, on separation, silicone can be detected on the surface of the adhesive. True, nontransfer of material from one surface to another is probably not achievable with a soft elastomeric film such as an unfilled silicone release coating. The questions, then become: What is acceptable? How will it be judged? How is that state of cure reached? Unfortunately, the answers are as varied as the applications. A few examples: For large labels applied to clean surfaces, quite large amounts of silicone transfer can be tolerated. For very small, stiff labels applied to curved surfaces, very little can be tolerated. For carbon-fiber pre-preg laminates, virtually no silicone transfer is acceptable.

Nor is silicone transfer the only measure of state of cure. In a polyfunctional system, even after prolonged heating, substantial numbers of unreacted, but reactive, groups still remain, unable to cure because of steric separation from the corresponding reactive group needed to effect cure; e.g., vinyl on polymer and SiH on crosslinker. Although to all intents and purposes the film may be cured, it is still reactive and not inert. This may lead to chemical reaction with materials subsequently brought into contact with it. This causes release level instability.

In the food industry, extraction of cured materials by water, alcohol, or hexane is often used to test inertness or cure. Zero extractable content is another result achieved asymptotically.

In the release of pressure-sensitive adhesives, it is often possible to plot cure temperature (for a constant exposure time) and release value. The point where these release values become constant could be interpreted as the minimum requirement for curing. Unfortunately, this point differs widely for different adhesives. Some examples are shown in Figure 7.

Points A, B and C could all represent a well-cured coating for the adhesive in question. All three may represent significantly more demanding conditions than are necessary for supermarket labels, and all three could be totally inadequate for a food-grade application. Thus, physical appearance (smear or no smear) may indicate cure – not too well in absolute terms, but well enough for, say, asphalt packaging.

Tape detackification, as a measure of migration, is a possibility; but percent extractability is more demanding and more quantitative. However, the question, “What is the acceptable limit,” is pertinent, as zero extractable will be nearly impossible to achieve if not to measure.

Release values are fine for a given circumstance but are a backward-looking measurement since, if the level is too high, the material made is wasted. Release stability is an excellent measure but, again, occurs too late to make an on-the-spot judgement. Silicone migration can be detected on adhesive surfaces by a number of means, and contact angle of wetting solutions is a quick, easy test which offers great possibilities.

However, it needs to be related to acceptable performance. Crosslink density measurements are a fine, fairly absolute indicator of cure, but the normal test methods are hopelessly cumbersome.

This leaves us in the real world where each coater uses one or a combination of these methods to make a judgement of the state of cure of a given silicone formulation and pronounces it fit or not for a given application. There is still room for much science here!

## Factors affecting release performance

Release performance is normally measured by the force necessary to remove an adherend from the release surface. It is quoted as a force per linear measurement, the latter being the width of the adherend at right angles to the direction of removal. This measurement is affected by a very large number of potential variables. These will be discussed under two headings: fundamental and practical. The former will include control of the elastic nature of the silicone, surface nature of the silicone, chemical type of the adhesive, elastic nature of the adhesive and other factors inherent in the materials. The latter heading will discuss the impact of delaminating speed and angle, and the effects of imperfect coverage of the substrate by the silicone. It will revisit the impact of state of cure, examine the impact of the thickness of both the silicone and adhesive layers, and look briefly at the impact of temperature and humidity on release performance.

### Fundamental factors inherent in the nature of the materials

One of the difficulties in writing an account such as this is that, viewed today, it ought to seem a coherent, logical deductive story. In reality, most of the progress has been made empirically; much research has gone to explain known phenomena and has rarely predicted new developments. This is particularly true in the fundamental work done on the nature of the materials and the impact on release performance.

The earliest solvent-based release coatings were based on a silanol end-stopped polydimethylsiloxane of about 5000 to 6000 siloxane units in length. Such a polymer is heavily coiled and not at all a long, thin, gently undulating “string,” although it is often portrayed as such. When such a polymer is crosslinked into a silicone elastomer, the long backbone is only attached to the matrix at each end. This provides a very large scope for deformation of the elastomer by displacing and straightening of the coils in the polymer chains. Thus, careful measurement will show that even a thoroughly cured coating of this nature will have an elongation at break of several hundred percent.

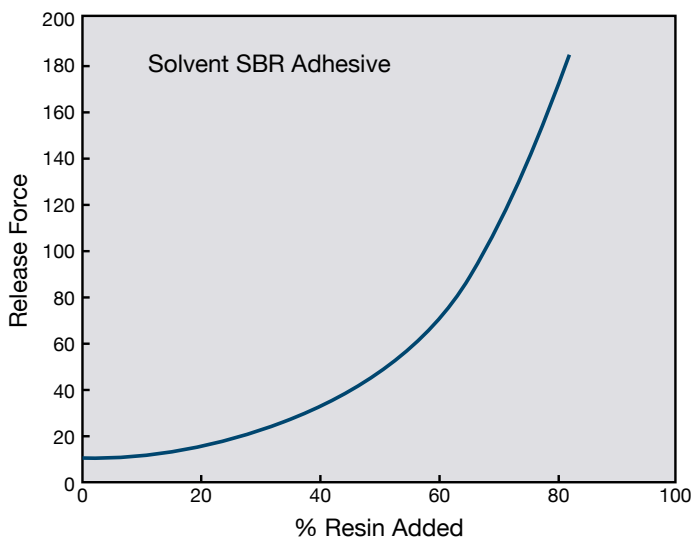
Later coatings were developed based on the same chemistry; the only difference was the free chain length, or molecular weight, of the silanol end-stopped polymers. Polymers of approximately 600 siloxane units and even 20 units were used. These coatings exhibited significantly different release performance – different not only in release value at a given peel rate but also very different in the relationship between release force and peel rate. (See Figure 8.)

These shorter chain length polymers have significantly less extensibility available than the long polymers. In practical terms, the highest-molecular-weight polymers give soft, very elastic coatings. The 600-unit or so polymers give fairly hard coatings with just a few percent, maybe 20 or so, elongation at break. The very short chain polymer gives a brittle coating that is almost inflexible without shattering, and elongation at break is too low to measure. Crosslink density measurements reveal magnitudes of difference between all three. From such empirical beginnings has developed an understanding of the rheological impact of both release coatings and adhesives on release performance.

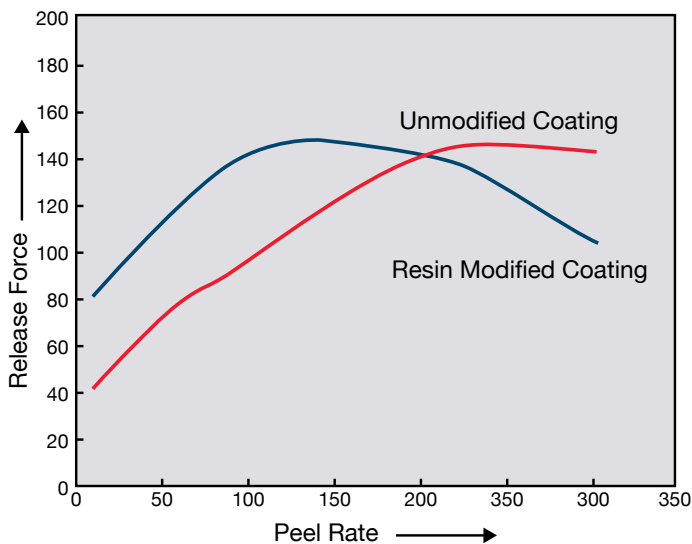
Although these condensation systems offered quite a wide range of release to accommodate a wide range of adhesive types, there was still a need for release values higher than those available from such systems. Incorporation of silicone resins was found to raise release values satisfactorily, at least at slow peel rates.

The impact of such resins was not linear, however, and the familiar hockey stick curve was developed to show the impact of resin addition. (See Figure 9.)

**Figure 9.** Effect on release values of adding resin to coating.



**Figure 10.** Comparative high-speed release profiles.



High-speed peel testing did not become generally available until the mid-1980s. Until that time, most release testing was done in the 6 to 600 inch per minute (ipm) range. Converting, printing and matrix removal in the label industry and slitting, rewind and end-use in the tape industry were done at speeds much higher than 600 ipm. This led to a situation where materials might test well but perform poorly in practice and vice versa. The use of resins as high-release additives was a good illustration. Addition of resins at a given level might increase release results quite satisfactorily at low peel rates, but the finished laminate might show no improvement at all in convertibility. Indeed, sometimes convertibility actually deteriorated. Given the advantage of today's high-speed peel testers we can now see why. (See Figure 10.)

The increase in release force at low peel rate is clear and unequivocal, but at high speeds, release is actually lower. It was many years before an understanding of this difference was forthcoming.

In the emulsion area, it was not possible to emulsify the highest-molecular-weight polymers, so only products based on lower-molecular-weight polymers were available. This did limit the performance range available to emulsion users. In addition, no satisfactory emulsion of the resin-based additives was offered.

With some additive chemistry already mentioned and some alternative tin-based catalysts, the condensation systems had reached the limit of their development. A range of different-molecular-weight silanol end-stopped polymers; a resin-based high-release additive; three or four organotin salt catalysts offering differing solubilities in various solvents, differing volatilities and differing cure rates; some fast-cure additives and an anchorage additive or two constituted the available options. This was true as much as 15 years ago and remains true today.

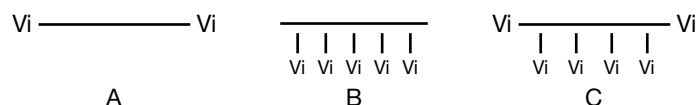
As environmental pressure against solvent emissions grew, the limitations of emulsion technology became more apparent, and attention turned to 100 percent solids or solventless systems. Condensation chemistry proved unable to meet the challenge, and addition chemistry was adopted. As stated earlier, this chemistry made it possible to make multifunctional polymers, not just end-stopped ones:



This had great implications for release control and cure rate improvement.

Initial work was concentrated on a solventless system. Condensing twenty years of development, both in release testing and materials, the situation today can be summarized as follows:

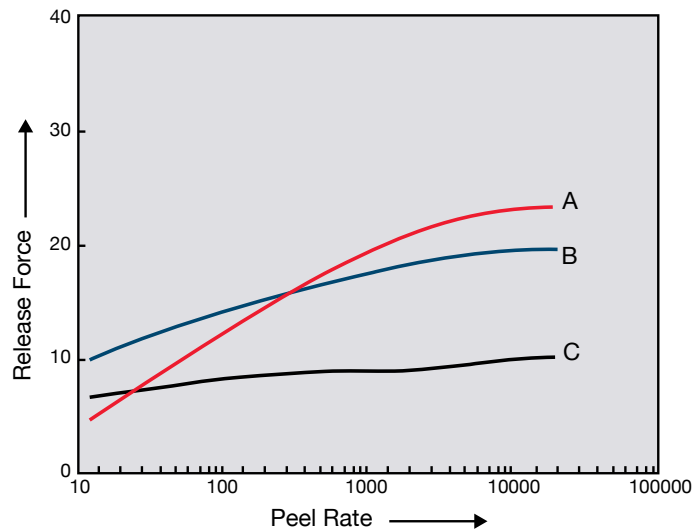
Polymers can be made with only terminal reactive groups, only side chain reactive groups or both:



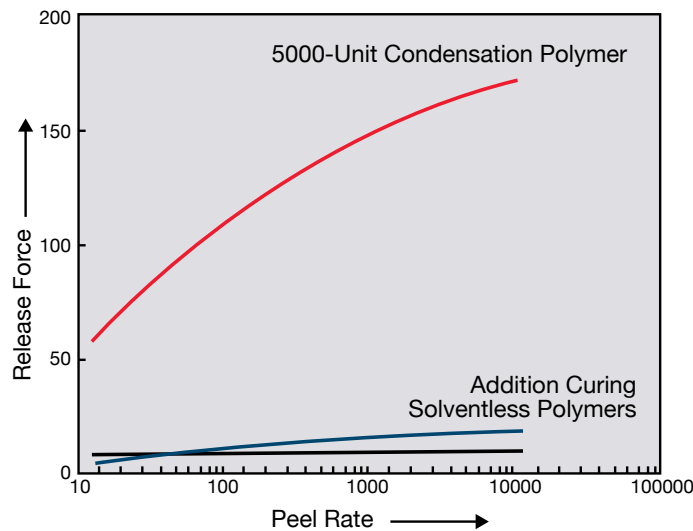
For a solventless system to be coatable on the roll coaters described earlier, it is desirable that the polymers should be no longer than approximately 300 siloxane units, and preferably in the 100- to 200-unit chain length range.

The release behavior of these polymers is illustrated in Figure 11. These differences, however, are relatively small compared with the range available in condensation solvent-based systems. (See Figure 12.)

**Figure 11.** Impact of polymer morphology on release profile.



**Figure 12.** Comparison of solvent-based and solventless polymers.



These graphs change significantly as the adhesive mass is changed, but the relationships remain reasonably constant. As can be seen in Figure 11, the terminal-functional solventless polymer “A” gives somewhat more elasticity than the multifunctional polymer “C,” but both give low release values and flat release value profiles with peel rate. After 30 years or so of condensation-based systems, the industry was attuned to a certain type of product; and the move to solventless did not fit well, as release values were generally too easy. The use of resin-based, high-release additives ceased to be a solution for special needs and became an essential component of most constructions. Unfortunately, the same tendencies persist even today. These resin-based materials work well at low peel rates but not so well at high rates.

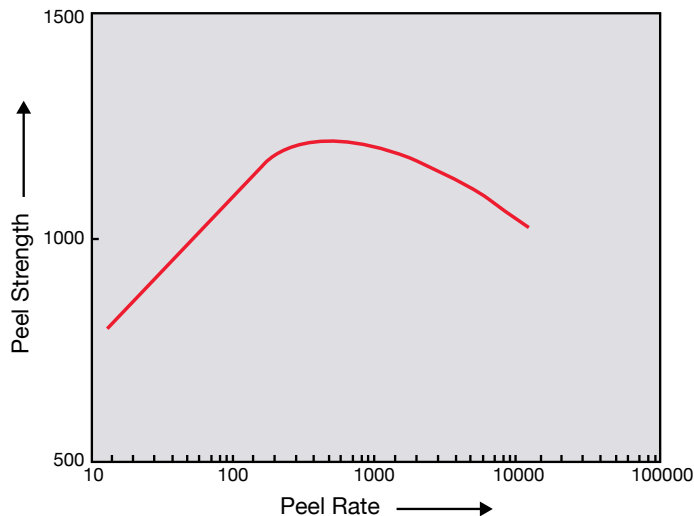
Fortunately, help was at hand. At the same time silicone release coatings were moving away from solvent, the same move was afoot in adhesives. Until the mid-1970s, solvent-based rubber adhesives were at least 80 percent of the label and tape industries. It proved impossible to either emulsify these materials or make a solventless version. Consequently, major changes in chemistry and materials were required. Two contenders emerged and still compete neck and neck today: water-based acrylic emulsions and rubber-based hot-melt adhesives. These have very different peel rate profiles than solvent-based rubber adhesives. It has been possible to marry the emergence of solventless silicone to water-based and hot melt adhesives and make products that satisfy market needs.

Solvent-based SBR adhesives, for example, are high-molecular-weight materials, most of which do not require curing, just solvent removal. The dry adhesive has both high physical strength and great elasticity. This shows in a peel rate/adhesive strength curve and also in a release force/peel rate curve. (See Figures 13 and 14.)

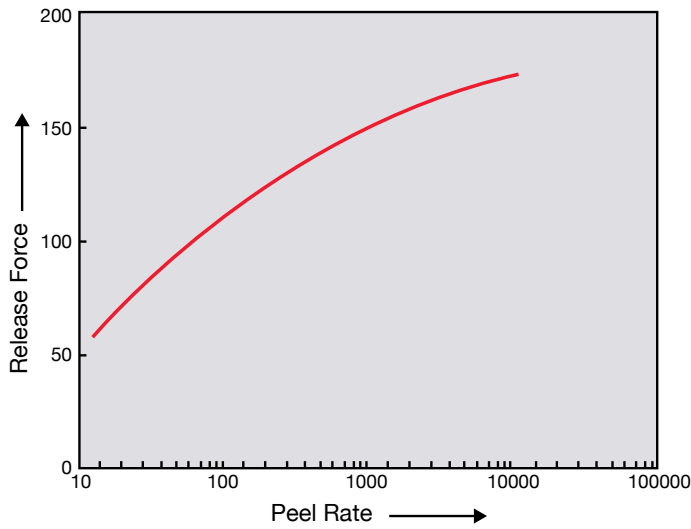
The water-based acrylic has greater elasticity but lower strength, and the hot-melt, vice versa. This yields the release force/peel rate comparisons shown in Figure 15. These are typical examples of adhesives released from a solventless release coating. Clearly, the need for high-release materials is greater for use with hot-melt adhesives than with water-based acrylic adhesives. This is true in practice as well as in theory.

In Figure 13 we can see the peel strength drop at a certain peel rate. This is normally explained in terms of Tg phenomena. Tg is usually thought of in terms of the transition from a glass-like state to a rubbery state as the temperature is raised. However, one can also encounter the same apparent state change when frequency is used instead of temperature. Most people are familiar with breaking thread by snatching instead of a steady pull. The molecules do not have time to relax and move around each other, so they break instead. A similar phenomenon occurs in adhesives, often accompanied by a significant amount of cohesive failure in addition to adhesive failure.

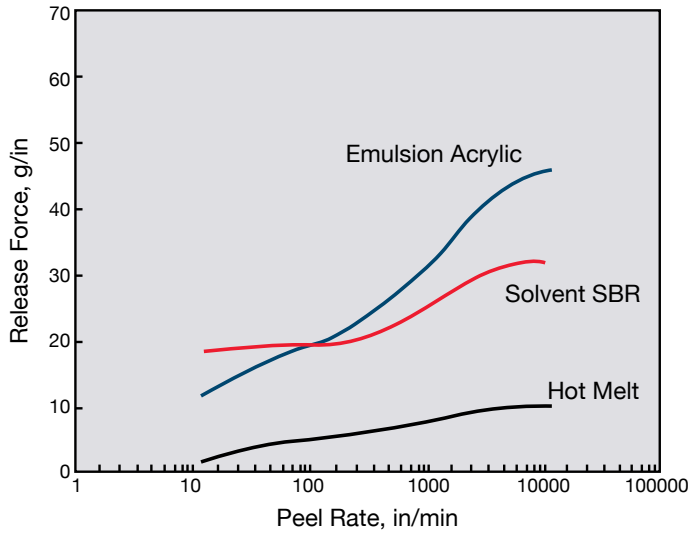
**Figure 13.** Solvent-based SBR adhesive – peel strength.



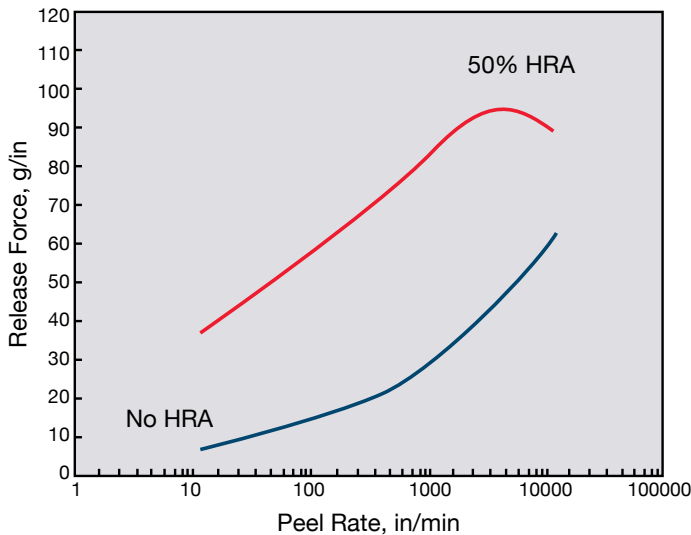
**Figure 14.** Solvent-based SBR adhesive – release force.



**Figure 15.** Typical release profiles for various adhesives.

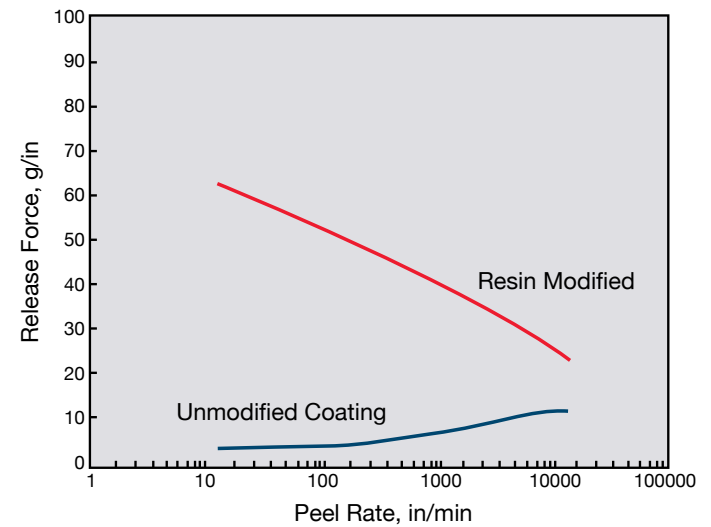


**Figure 16.** Release profiles with water-based acrylic adhesive.



This is not a treatise on adhesives or physics, but some discussion is necessary since precisely the same phenomenon is occurring in the silicone release coating as peel rates are increased. The change from rubbery behavior to glass-like behavior in adhesives is very often marked, in the practical sense, by a change from smooth, quiet release to raspy, noisy release. This phenomenon is particularly common in hot-melt adhesives, which just happen to have a high Tg! It is not nearly so marked in water-based emulsions, particularly acrylics, and is pretty much a rarity in a pure polymer-based release coating. However, the resins used as high-release additives are typically solids, even at high temperature, and are particularly hard and glass-like. Incorporating these resins into a release coating effectively raises the Tg of the cured coating. Thus, even water-based acrylic adhesives may show the onset of raspy release – not exhibited in the absence of the resin additive – at elevated peel speeds. Hot-melt adhesives will, therefore, present a major problem with a resin-containing release coating if raspy, noisy release is to be avoided. Figure 16 and 17 illustrate.

**Figure 17.** Impact of resin on release profile of a hot-melt adhesive.



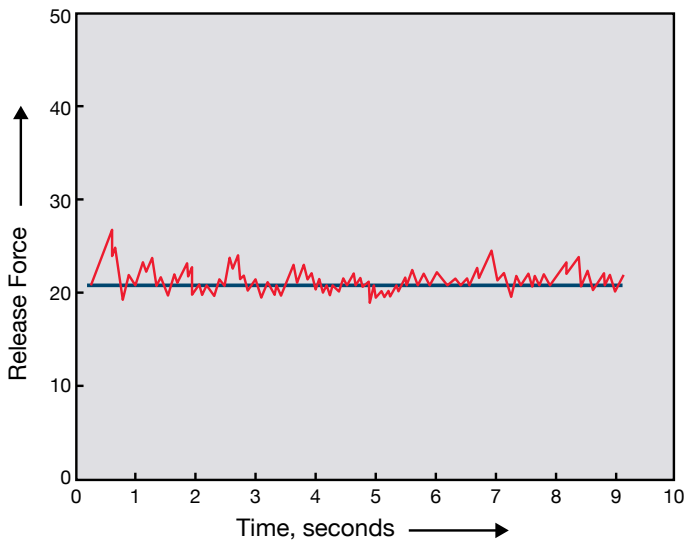
Continuous monitoring of a release force measurement can be even more revealing. Figure 18 shows a water-based acrylic releasing from a solventless release coating with no resin high-release additive.

Figure 19 shows a hot-melt adhesive releasing from a coating with about 25 percent resin. Both are at 10 meters per minute peel rate.

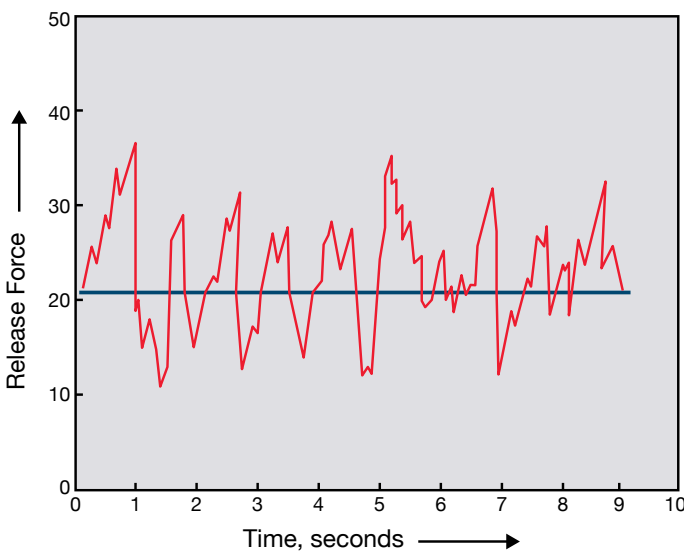
Figure 18 represents smooth, quiet release, and Figure 19 raspy, noisy release. The noisy release is associated with cohesive fracture of both the silicone coating and the adhesive. It is due to the more glass-like behavior of the materials at this frequency than that of the lower Tg (and hence more rubbery) materials in Figure 18.

The question remains, “Why do these resins raise release at low peel rates?”

**Figure 18.** Water-based acrylic release test.



**Figure 19.** Hot-melt adhesive release test.

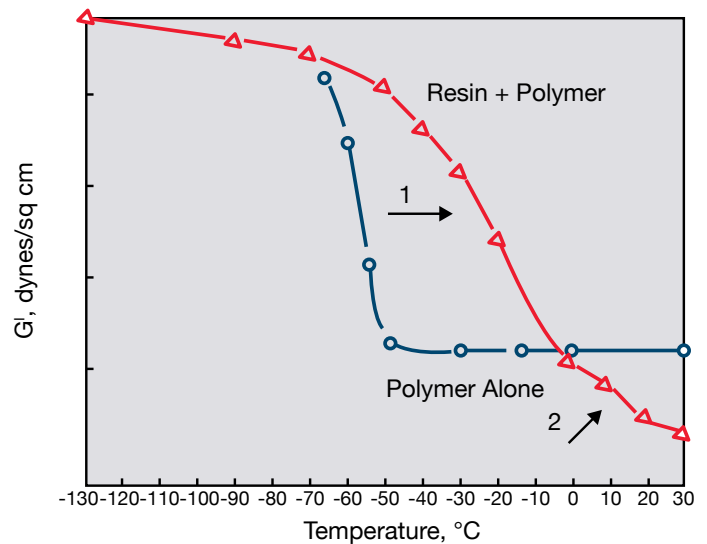


We have seen why resin effectiveness is greatly reduced at higher peel rates. The answer to our question is not absolutely clear, but it does seem that the rubbery nature of the crosslinked polymer is altered by the resin, which acts as a small particle filler. The rubbery plateau of the coating is moved to another domain, and this may be the major effect. Certainly, the cohesive strength of the silicone film is increased by resin incorporation. Figure 20 shows the change in “rubbery plateau.”

Returning now to the addition-cured polymers: clearly, the multifunctional polymer will produce a higher crosslink density than the terminal-only polymer. This will alter the basic nature of an unmodified coating somewhat, the multifunctional polymer being more glass-like than the end-functional one. This difference will then accentuate the resin tendencies.

However, release values, profiles and their control are not the only factors to be considered when formulating release coatings. These other factors, which will sometimes be in conflict with pure release considerations, will be examined under the heading “Formulating Release Coatings.”

**Figure 20.** Effect of resin on storage modulus of lightly crosslinked polymer systems.



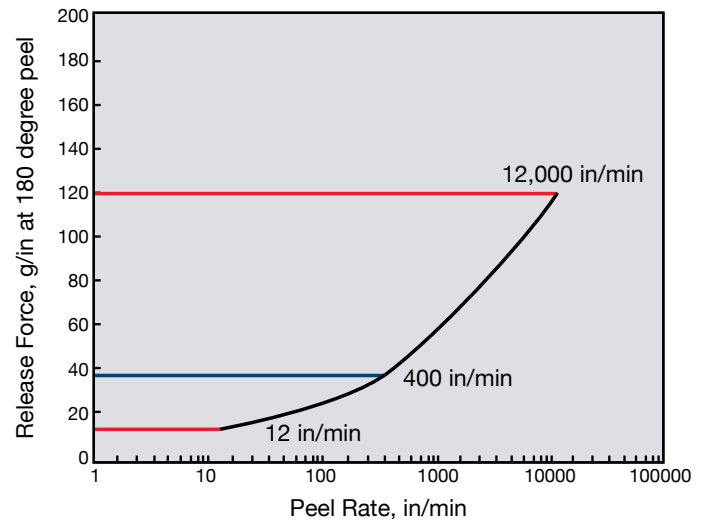
### The practical control of release performance

To obtain some kind of benchmark, consider one coating type for a while. It makes no great difference whether it is an emulsion, solvent-based or solventless type. Some factors affecting release are the same for all three.

The relationship between release forces and peel rate has already been mentioned. Figure 21 can be taken as typical.

Clearly, measurement at 12 ipm (0.3 meters per minute [mpm]), 400 ipm (10 mpm) or 12,000 ipm (300 mpm) will give very different release values.

**Figure 21.** A typical release profile.



Just how different will depend upon the adhesive above all, the silicone and some other factors, too.

The most important of these other factors is the angle at which the adherend is pulled from the release surface. If a pressure-sensitive laminate is pulled apart in a free-hanging unsupported state (Figure 22), the angle between the two substrates will reach a value that minimizes the force applied.

Figure 22.

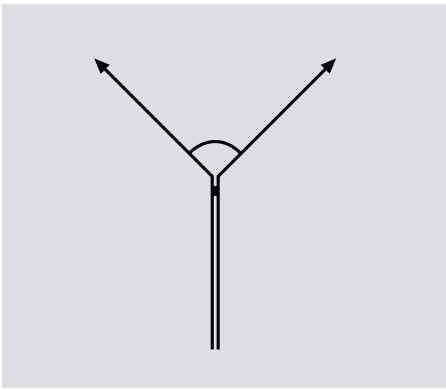


Figure 23.

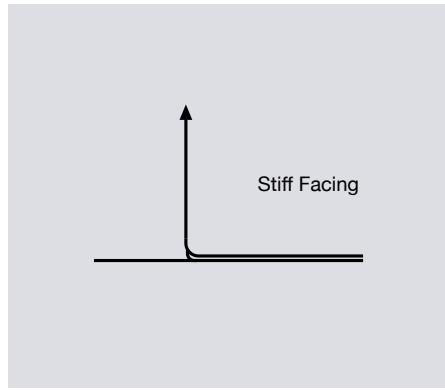
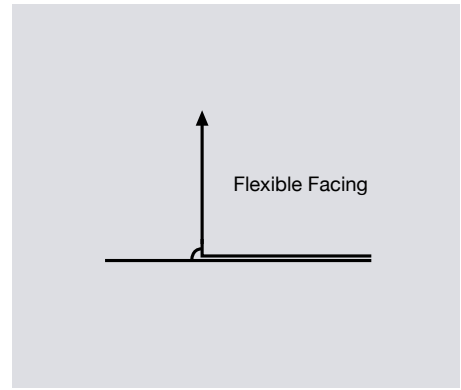


Figure 24.



In matrix removal operations on the press, this angle is often controlled to give smooth removal. In release testing, the angle is fixed, either at 90 or 180 degrees. At least that is the intent. In reality, due to the stiffness of both substrates, the angle is significantly less than 90 or 180 degrees. (See Figures 23 and 24.)

Figure 25. Effect of humidity on release values.

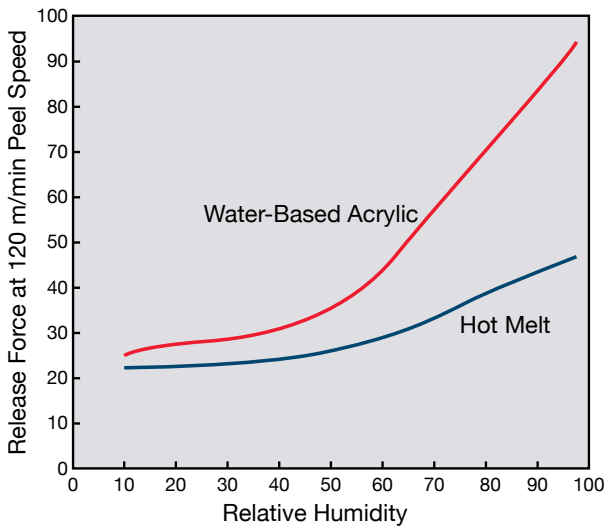
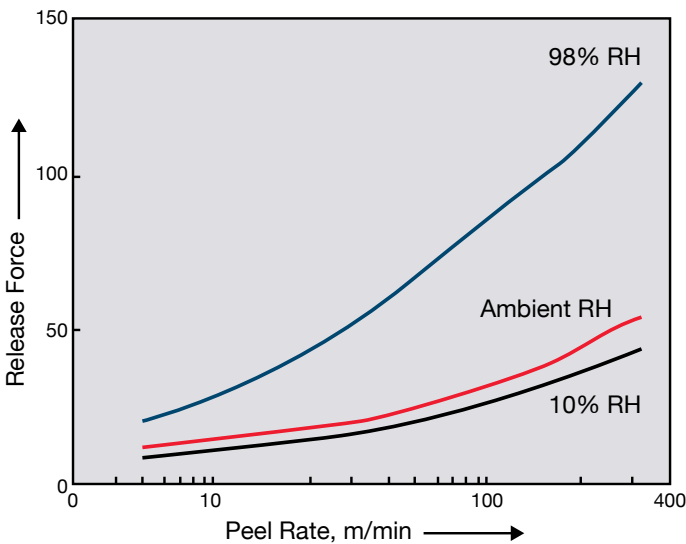


Figure 26. Effect of humidity on release profile of an emulsion acrylic adhesive-based laminate made with paper backing and facing.



So, substrate basis weight, and subsequent stiffness, is a major variable. Furthermore, in reality on the press, both label stock and liner are pulled, whereas in testing, either one of the other is pulled. A major influence on stiffness of paper substrates, which are by far the major proportion of the market, is humidity. Figure 25 shows the impact of humidity on release force, and Figure 26 shows the impact on release profile.

Temperature will affect the rheological state of the adhesive, in particular, and also the state of the silicone and substrates. Clearly, for release testing, temperature and humidity are major variables in addition to peel rate and peel angle.

Although the effect of these variables has been discussed from a release testing standpoint, they do have the same influence in practical use. For example, asphalt is easily removed from release liner when cold and hard, but removal becomes increasingly difficult as the asphalt becomes more rubbery. A further example is the conversion of a given laminate for different size labels. Large labels usually convert and matrix strip easily; but the same material, when used to make very small labels may prove too stiff, and the labels will fit off as the laminate moves over small-diameter rollers. (See Figure 27.)

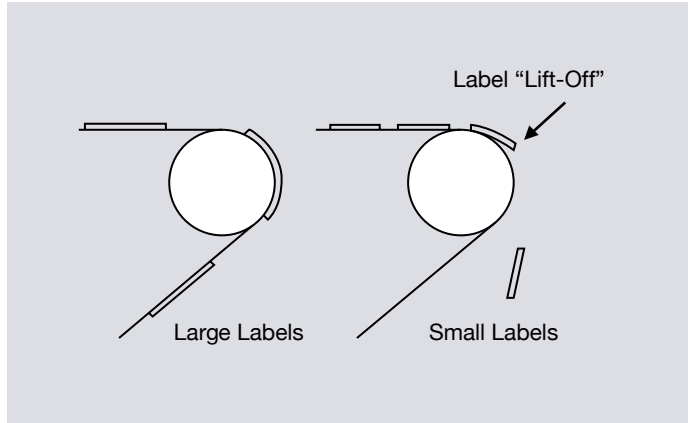
Another major factor affecting release is the degree of silicone coverage of the base liner. If greater or larger portions of the base are left either uncoated or incompletely coated, the adhesive will contact the base, and release values will be both higher and less stable with time. Coverage assessment will be examined under "Testing."

Adhesive and silicone coating thickness also affect release force measurement. These effects are simply observed. The greater the thickness of either, the greater their energy-absorbing capabilities as they stretch and, thus, the higher the release forces required. However, for stiff, fairly inelastic examples, the impact may be very small. Figure 28 shows the impact of coat weight (or layer thickness) on release values for some silicones. "A" represents the amount necessary for total coverage – less allows paper fibers to impact release values. Figure 29 shows how adhesive thickness affects release force.

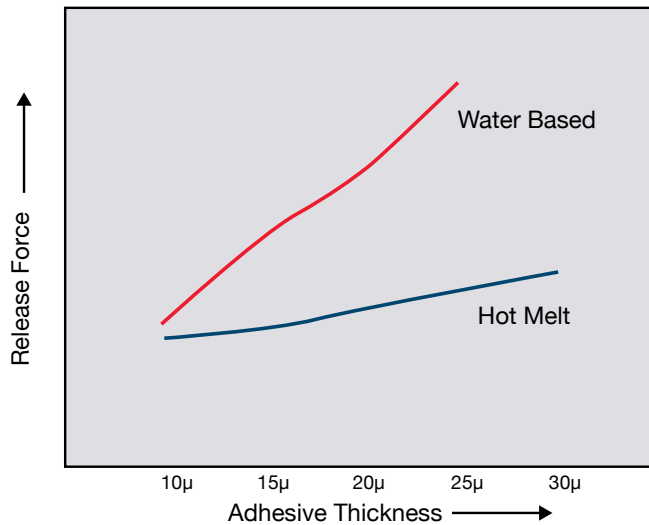
Now it is time to re-examine state of cure. If a coating is "fully cured," whatever that means, it should reach a state of constant physical parameters in terms of hardness, elasticity, strength, etc., and hopefully, inertness. Release performance should also be consistent and repeatable, and release values should be stable. This state is easier to achieve with some polymer types than

others. Also, some adhesives can tolerate significant undercure, while others cannot. Since such a taste of “total” cure is achieved at the cost of long exposure to curing stimulation, be it thermal or radiation, the substrate itself may suffer significantly in terms of impoverished physical properties. Thus, such a state of cure is not always desirable. In reality, very few release coatings are cured to such a state, and all are undercured to some degree or other.

**Figure 27.**



**Figure 28.** Effect of film thickness on release.



What, then, is the impact of this undercure? The answer is totally adhesive dependent. Most rubber-based adhesives, solvent or hot melt, are relatively inert to unreacted reactive groups in the silicone. On the other hand, crosslinkable solvent acrylic adhesives can and do react strongly with SiH functionality in the silicone. This phenomenon is known as acrylic lock-up. Most water-based adhesives, either acrylic or rubber-based, exhibit similar tendency but to a lesser degree. With undercured silicone, release forces may be a little higher with even inert adhesives, simply because the elasticity of the silicone is higher due to a lower crosslink density or, easier said, a softer silicone.

For any given construction, there is a minimum degree of cure that will produce an acceptable product. This degree of cure is usually the point most users achieve, and any greater curing effort is perceived as a threat to the substrate. Release stability will always be improved with improved curing, and release

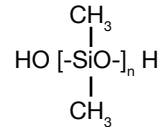
values will usually be lower. Other properties such as adhesive tack, subsequent adhesive strength and extractable content of the silicone film will all improve with better curing.

In summary, the major factors affecting release were brought together under two headings. The basic chemistry, coating methods, and the decisive influence of curing were reviewed. Coating formulation and the building blocks used will now be discussed.

## Formulating release coatings

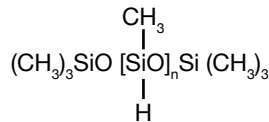
### Condensation type

#### Basic polymers:



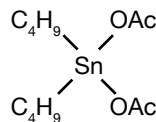
Where n ranges from ~20 to ~6000.

#### Crosslinkers:



Where n is ~40.

#### Catalysts:



Where OAc can be laurate, hexanoate, acetate, etc.

#### Fast-cure additives:



Where R is of a type such as  $\text{CH}_2\text{CH}_2\text{OCH}_3$ , etc.

#### Anchorage additives:

Epoxy-functional materials.

#### High-release additives:

Resin-based of the so-called M:Q resin type.

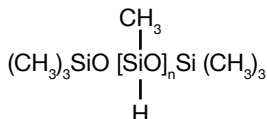
The selections made will reflect the desired release performance. The basic polymers range from low-viscosity fluids, where  $n \sim 20$ , to thick gums, where  $n \sim 6000$ . While permitting release force variation, the problem of solvent dispersion soak-in becomes more severe as the polymer molecular weight is reduced. Blends of these polymers are usually used whenever the 20-unit polymer is involved. Use of low-molecular-weight polymers is better suited to substrates with excellent holdout such as polycoated kraft or films. Cure rates differ somewhat, but all will cure at room temperature after solvent removal. Catalyst choice will be a reflection of solvent choice, oven temperatures and regulatory status. Anchorage additives are occasionally necessary on some substrates. They do not function on polyolefinic surfaces.

In the emulsion field, the lower-molecular-weight polymers can be mechanically emulsified as can the more hydrolytically stable catalysts. Emulsion systems do not have fast-cure additives or good high-release additives, but often they do not need them; and they do enjoy the ability to be used with water-soluble organics such as polyvinyl alcohol, carboxymethyl cellulose, starch and a host of others. They can also be used together with other organic emulsions such as polyethylene emulsion. This opens up significant opportunities not open to solvent-based materials.

## Addition cured materials

### Basic polymers:

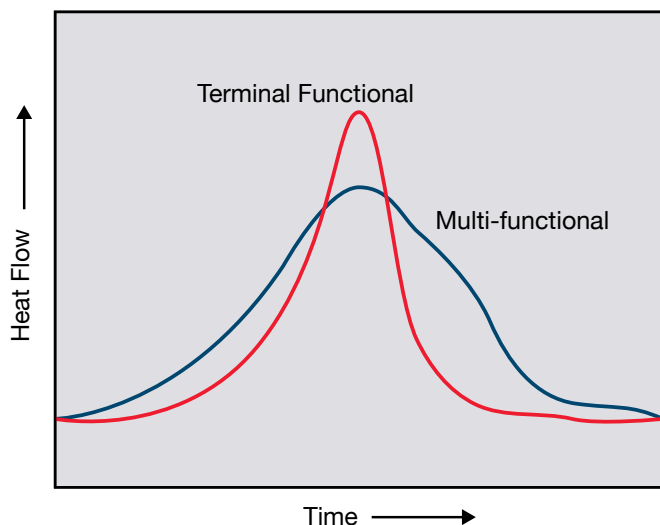
Both terminal and multifunctional vinyl polymers.



Where  $n+m$  ranges from 100 to 5000, and  $n$  ranges from 96 to 100 mole percent (i.e., no side chain – terminal only).

Normally, in solvent products, high-molecular-weight gums with side-chain vinyl groups are used. Solventless and emulsion products use much lower-molecular-weight materials and will use both terminal-only and multifunctional polymers. The influence of these on release has been discussed, but there are several other implications, also. In a polymer with five or six reactive groups, only one need react to tie the polymer into the gel. If the polymer has only two reactive groups, one must still react. So, in one case, one in five or six must react; in the other, one in two. This reflects itself in several ways, but the most obvious is in percent extractable material at various states of cure. Both kinds of polymer can be cured to very low extractables, but for any given set of cure conditions, the multifunctional polymer will show less extractables. This is an indication of cure rate. However, other indicators will show that the terminal-functional-only polymers reach completion faster – stability of release with a solvent crosslinkable acrylic adhesive, for instance, or differential scanning calorimetry (DSC). (See Figure 30.)

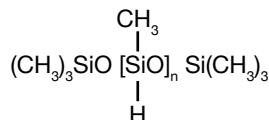
**Figure 30.** Differential scanning calorimeter trace.



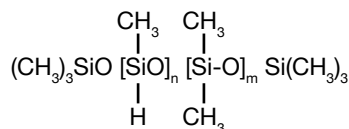
So, as in most aspects of release coatings, things are different, not necessarily better or worse. The use of a multifunctional or terminal-functional polymer as the basis for a solventless or emulsion addition-curing coating is very much a question of suitability to specific needs. Apart from functional issues such as curing and release properties, other issues such as working life, coatability and cost are relevant to the polymer section. Today, with a range of inhibitors, bath life is only a problem under special circumstances (one of which is gravure clogging), but coatability merits a few words. Differences between various polymers can be seen in coverage efficiency, leveling speed (removal of film splitting lines), gravure cell filling and emptying, and in the development of a fine mist or spray around the final transfer nip where silicone is actually laid onto the substrate. These differences are often as much a function of polymer molecular weight as of polymer architecture, but multi- and terminal-functional polymers do exhibit differences.

### Crosslinkers:

Both homo- and co-polymers of SiH functionality are used.



**Type A**



**Type B**

Homopolymer “A” is chosen for rapid gelation, good anchorage to substrates and good cohesive strength in cured film.  $n$  ranges from 5 to 60.

Copolymer “B” is chosen for good bath life and good final cure characteristics.  $n+m$  ranges from 5 to 60, and  $m$  from 50 to 90 mole percent.

Blends of “A” and “B” types are often used to blend properties. In solvent-based materials, “B” exhibits poorer anchorage properties than “A” and is not widely used.

### Catalysts:

Noble metal organo complexes are used. To improve solubility in 100 percent silicone systems, these are usually platinum or rhodium organosilicone complexes. In solvent-based products, nonsilicone complexes can be used. The normal level is 50 to 150 ppm platinum metal, based on total silicone content.

### Inhibitors:

These were listed under the chemistry section, but suffice it to say, some inhibitors can be packaged together with the catalyst with no damaging effects. Others, such as acetylenic alcohols, cannot. Inhibitors usually range from strong inhibitors with long, stable control on the bath life, but higher initiation temperatures, to low-initiation-temperature inhibitors with barely adequate



low-temperature inhibiting properties. Solubility in 100 percent silicone systems is always a concern, and often low-temperature storage of formulated products can cause the inhibitors to come out of solution.

In solvent-based systems, a wider range and greater concentrations are possible, so often spectacular curing performance can be coupled with good working bath life. Also, inhibitors can be blended to combine properties.

In emulsions, the separation of catalyst, polymer and crosslinker is easily achieved via separate oil-phase particles. Addition curing emulsions offer some very interesting capabilities, usually consisting of the same basic materials as solventless silicones.

#### High-release additives:

These are essentially the same kind of resinous materials used in condensation systems, but with the added advantage of being functionalized. Since they are solids, soluble in hydrocarbon solvents, their use in solvent-based materials is straightforward. For emulsions and solventless materials, however, they must be dispersed in a silicone polymer. This automatically limits the amount of resin that can be incorporated into a coating, since the polymer is added simultaneously. If the resin content is too high in solventless systems, coating problems arise as the viscosity rises rapidly with resin content.

Studies of resin molecular weight, type and functionality have shown some impact on the efficiency of raising release, but the significance is minor compared with the effect of resin concentration. The efficacy of high-release additives is a major concern in both emulsion and solventless areas.

In concentrating on solventless silicones, I have reflected the current state of the market, but solvent-based systems do merit further consideration. In both condensation and addition-curing systems, the choice of solvent used for coating is a critical factor. The solvent controls the overall density of the coating solution. This needs remembering since, while the coating mix is most often made up by weight all coating methods lay down a volume.

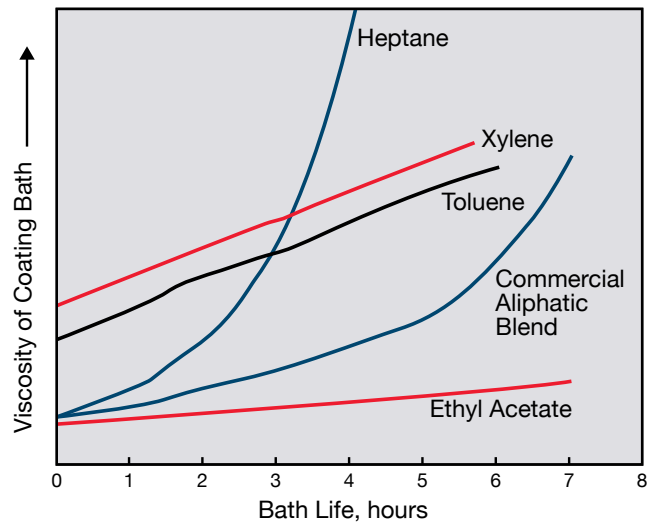
The spreading or wetting of the coating solution on various substrates is a critical factor in achieving both good coverage and anchorage. Solvents with a surface tension below that of silicone (21 to 22 dynes per cm) will spread and wet well on most substrates. Thus, hexane and heptane are good wetting solvents and will coat all molecular-weight silicone polymers well. Toluene will not, and anchorage is often a problem; on low-energy substrates such as polyolefins, beading up or reticulation is a major problem.

Use of low-molecular-weight silicone polymers exacerbates this problem. Mixtures of solvents can be used to advantage, as heptane is sometimes a little too volatile for use alone.

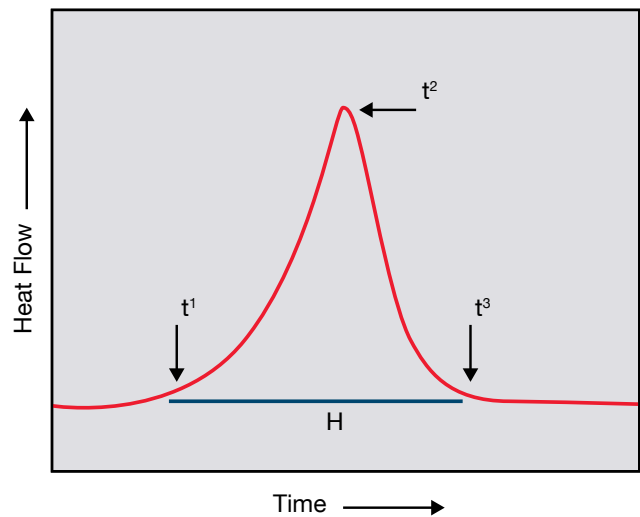
In addition to wetting and spreading difficulties, bath life can be very much affected by solvent choice. This is true both for condensation and addition types.

Figure 31 illustrates rate of increase in viscosity for an addition-cured silicone coating system in various solvents. Usually, there is a practical viscosity limit for gravure or Mayer rod coating. Thus, solvent choice greatly influences bath life.

**Figure 31.** Effect of solvent choice on bath viscosity with aging.



**Figure 32.** Differential scanning calorimeter (DSC) trace.



The use of solventless systems out of solvent is quite common. The disadvantages are that such low-molecular-weight materials give very low-viscosity coating solutions, and penetration into the substrates is a major problem. Also, such low viscosities can make the actual coating process a really messy operation. However, one can lay down very thin coatings of solventless silicones, which is desirable for film coating, for example, but solvent choice is critical.

Some solvents lend themselves much better to solvent recovery than others. Some solvents are nonflammable, and are attractive as such. However, if an optimum job of siliconizing is to be done, these kinds of considerations must come second to the effectiveness of the solvent as a coating, curing and bath medium.

## Testing

This subject is easily divided into two approaches: testing of the raw materials before use and testing of finished products.

### Raw materials

Only silicone release coatings will be addressed, not substrates and adhesives.

Silicones can be measured physically; e.g., viscosity, specific gravity, nonvolatile content, percent vinyl, hydride, silanol, alkoxide, etc. These are important tests related to consistency; they tell us nothing about functional stability. The two major areas of functional suitability are ability to cure and release performance.

Cure rate can be examined by coating onto a chosen substrate and curing in an oven, then measuring cure by one of the methods already discussed. This is a very subjective test, but can be quite useful. More recent tests that are much more objective are becoming widespread. However, the relationship between the test and real use is very much debatable.

Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) are both finding support. The first measures the heat given out by an exothermic curing reaction. The second follows the development of mechanical strength as a system cures or hardens. A typical trace is shown in Figure 32 (page 17).

- $t^1$  is the onset time (temperature).
- $t^2$  is the time (temperature) at which the maximum heat flow is reached.
- $t^3$  is the time (temperature) at which cure is complete.
- "H," the area under the curve, is the total heat given out during curing.

Figure 30 (page 16) showed the difference expected between a highly functional polymer and a terminal-only functional polymer. The DSC is a wonderful tool for examining consistency, but the relationship of any of these parameters to functional suitability of a release coating is difficult to see. Certainly, a smooth, rapid decline from  $t^2$  to  $t^3$  is indicative of a "finished" cure. However, since a large number of very commercially successful coatings do not show this, a little uncertainty exists. Further, some coatings are seen to have higher initial, peak and finish temperatures and yet clearly show faster cure on a machine in terms of release stability, extractable content and loop tack. No doubt, time will improve the usefulness of the information provided by DSC.

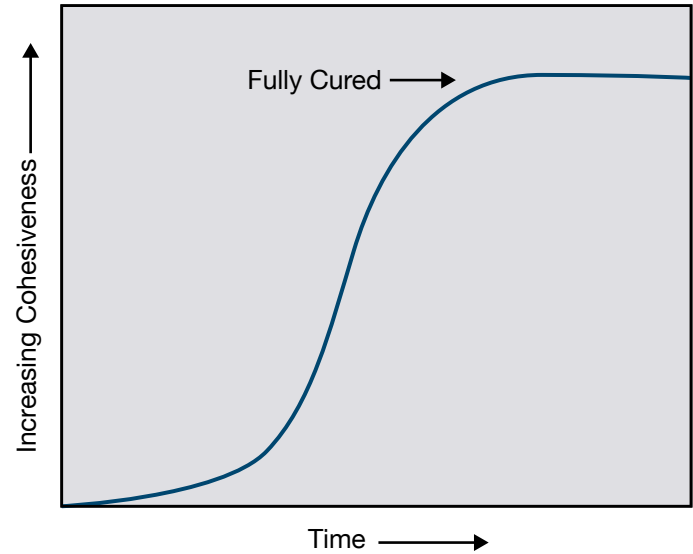
DMA is a little easier to envision. A liquid sample ends up as a lump of cured elastomer. Progress is monitored along the way. A number of devices exist that can do this with varying sophistication and cost. A typical trace is illustrated in Figure 33.

It is useful to look at two systems here – the terminal-functional polymer and the multifunctional polymer. (See Figure 34.)

This is an intriguing difference and mirrors cure data provided by acrylic adhesive compatibility, for instance. Recent work done with the vibrating needle curemeter<sup>1</sup> (VNC – a simple form of DMA) has begun to show the relationship between rheological properties and release properties, and to offer hope of release performance prediction before coating and curing. The VNC offers information on both cure rate and release value

and so is of great interest.

**Figure 33.** Development of cohesive properties with time (curing).



**Figure 34.** Comparative DMA of terminal and multifunctional polymers.

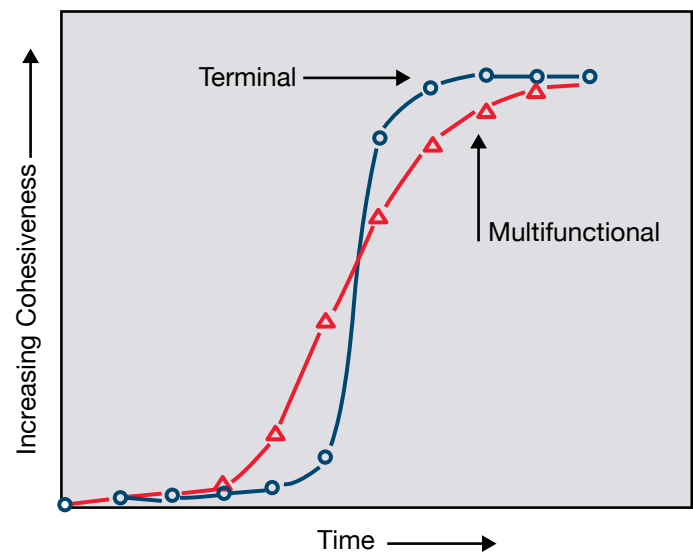
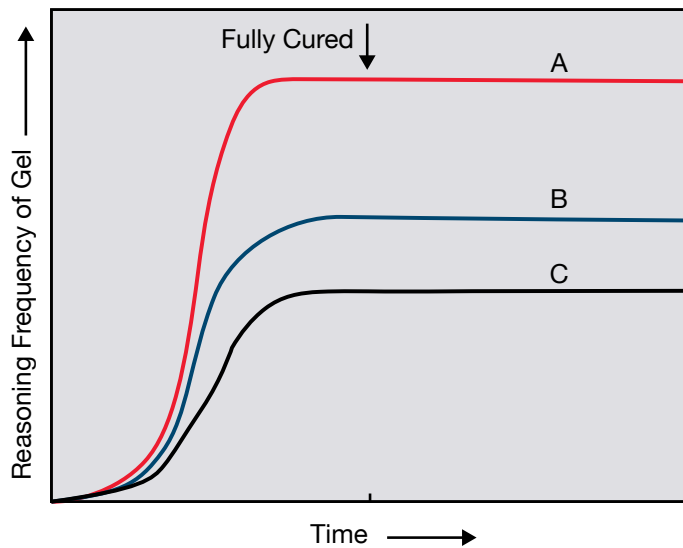


Figure 35 shows a series of VNC curves. Curve "A" represents a system that is curing into a tightly crosslinked gel. Such a system uses either a very short chain terminal-functional polymer, or a multifunctional polymer with several reactive groups along the chain – two or three per hundred siloxane units. Such a system is hard and brittle when cured and will give very flat release force versus delaminating speed profiles. Curve "C" represents a system that is soft when cured. Such a system uses a terminal-functional polymer, one with no side chain functionality. This type of cured film offers rising profiles of release force and speed and will tend to give smooth, quiet release with hard adhesives. The release characteristics are predictable from the final resonating frequency of the gel. The cure rate prediction comes from the rate of rise from the liquid state to the cured gel state. In this case, it is clear that "A" rises more rapidly than "C." In reality, multifunctional polymers do gel more quickly than terminal-functional-only polymers. Thus, the VNC curves enable

us to predict, at least to some extent, the cure rate and release values of the two polymer systems. Curve “B” represents an intermediate state between “A” and “C.” Such a system could come from either a low-viscosity terminal polymer or a polymer of reasonably long chain length with just one or two reactive groups per hundred siloxane units along the chain.

**Figure 35.** Development of adhesive properties with time (curing).



A very similar set of curves can be produced by the incorporation of high-release additives into any given polymer system. Since the resins are generally solids, they are seen by the VNC as very highly crosslinked species, and even modest levels of resin will greatly increase the hardness of even the softest cured polymer films. The impact on release profiles has been discussed earlier. The VNC offers a somewhat predictive insight into the use of high-release additives in various polymers.

Neither the DSC nor the DMA methods have gained wide acceptance for testing yet, but they show great promise. Neither is suitable for solvent-based or emulsion systems.

Release testing before use is clearly a contentious subject, since substrate, curing conditions, adhesive and test conditions will all need to be tightly controlled if such testing is to be meaningful. Mostly, the preference is to examine other parameters and trust that release will be in specification.

Release testing of the finished product, laminate, tape, etc., is another matter and is a fundamental activity.

### Finished product testing

First, consider silicone-coated liner. Tests of relevance include coverage, coat weight and state of cure.

Coverage is easily tested on paper substrates by one of a number of dye stain methods. Essentially, such a stain colors the paper and not the silicone. Noncovered areas are easily seen. However, just how complete coverage needs to be to provide acceptable performance is somewhat more subjective. It is not difficult, however, to provide a dye stain “standards” match to release performance.

Coat weight measurement is very easy today, thanks to the emergence of benchtop x-ray fluorescence units that accurately

measure silicon content. To turn this coat weight, however, known standard coat weights are needed, so the instrument is only as good as its standardization. Nevertheless, these instruments have wrought a mini-revolution in the silicone release coating industry. Other methods to exist based on other forms of detection, but are not widespread. Further methods based on a usage can also act as a broad check.

In addition to being used for releasing adhesive masses, release liners are used for oil and water repellency, release of foodstuffs, industrial resins, sealant and caulk masses, asphalt, synthetic leather and clothing materials, and as barriers to liquids. Testing for such applications is as varied as the applications themselves and cannot be covered here.

### System choice

The choice among solvent-based, emulsion or solventless systems is very much dependent on the needs of the occasion, both in terms of processing and product performance. (See Figure 36.) In today’s market, more than 65 percent of siliconizing is done with solventless. Ten years ago, less than 15 percent was solventless.

Looking at the various market segments, the label industry today is dominated by solventless siliconizing. The tape industry draws on all three, but solvent-based coating does offer some advantages in terms of smooth rewinding. In the non-pressure-sensitive sector, the food and packaging segment uses mostly emulsion-coated silicone, and solventless has a surprisingly small share. What does the future hold?

### Future developments

Today, little or not development is being done on condensation-curing systems. We may be nearing the limits of thermal-curing addition systems, as well, although new catalysts and inhibitors are still very much sought after. Faster-curing systems that yield more inert cured films are the goal. Emulsion systems have some way to go to catch up to solventless, so improvements are likely there; and the dream of an all-water-based facility is still real. At present, such facilities have lower productivity than solventless/hot-melt setups.

Radiation curing has been around for a while now and has generally proved disappointing. Why? In non-release fields, radiation curing produces beautiful, glossy coatings with millisecond cures. In the release field, needs for both a high dimethyl content and a reasonable degree of elasticity have produced release coatings with raspy, noisy release, much slower cure rate than their organic counterparts, and some release stability problems. Eventually, all these issues will be resolved, but not in the short term. Perhaps, significant changes in adhesives will rescue this kind of hard, inelastic coating, as happened for thermal solventless. True UV curing has not yet arrived. We do have UV-initiated epoxy ring opening curing, but catalysts continue to be a challenge. EB curing faltered on the dual problems of equipment costs and inerting costs.

An EB system that did not require inerting would be a big step forward. Current chemistry does not hold out much promise; but there is much activity in other, nonsilicone fields, and some may be transferable to release coatings. Certainly, the complete absence of post-cure inherent in EB treatment is a big attraction.

**Figure 36.** Advantages/disadvantages of solvent-based, emulsion and solventless systems.

Advantages	Disadvantages
<b>Solvent-based:</b>	
<ul style="list-style-type: none"> <li>• Very accurate coating control, both in terms of the coverage and coat weight</li> <li>• Wide range of products, both addition and condensation curing</li> <li>• Fast, low-temperature cure capability</li> <li>• Can be used for a very wide range of substrates</li> <li>• Good release profile range</li> </ul>	<ul style="list-style-type: none"> <li>• EPA and flammability problems; need either solvent recovery or incineration (both costly)</li> <li>• Difficulties with release control for tight release</li> </ul>
<b>Emulsion:</b>	
<ul style="list-style-type: none"> <li>• Water-based (nonflammable)</li> <li>• Wide range of organic materials available with which to blend (both soluble and latex)</li> <li>• Excellent coating control</li> <li>• Coatable by a wide range of methods</li> </ul>	<ul style="list-style-type: none"> <li>• Water-based; damages paper</li> <li>• Difficult to coat plastic substrates</li> <li>• More difficult to use on heat-sensitive substrates</li> <li>• Materials susceptible to freeze-thaw damage</li> <li>• Drying and curing more demanding than other systems</li> <li>• Tight release control difficult</li> </ul>
<b>Solventless:</b>	
<ul style="list-style-type: none"> <li>• No EPA problems</li> <li>• No solvent costs or concerns</li> <li>• Current technology</li> <li>• No flammability problems</li> <li>• Curing cycle is the easiest of the three systems</li> </ul>	<ul style="list-style-type: none"> <li>• Coating difficulties                             <ul style="list-style-type: none"> <li>– Special coating head required</li> <li>– Get higher coat weights</li> <li>– Coverage concerns</li> </ul> </li> <li>• Tight release control is most difficult of the three</li> <li>• Need higher base paper quality</li> </ul>

Finally, in all of these systems, the most pressing needs is still better release control. The move to solventless brought very easy release and flat release force/peel rate profiles, effectively lowering the bottom end of the release-force spectrum but, at the same time, putting the high end further away. Release-force elevation with resins is still the only half-way decent method, and it is not at all satisfactory in meeting all market needs. The need is for a system that is equally effective at all peel rates, which will reach out to the 20 to 30 times base level instead of today's 10 to 15 (if we are lucky). We need a system that works well with all adhesives and does not impair anchorage or cure rate, or produce raspy, noisy release.

So, as we look to the future in conventional coatings, improved release control might be the most desirable single development. Improved radiation curing systems and improved coating methods may also appear.

What of nonconventional developments? Several come to mind:

- Plastic release liners made by extrusion of, say, polyolefin and silicone – no coating involved

- Non silicone release coatings (difficult for me to imagine, but certainly possible, especially with eutectic mixtures of various polyolefins) designed to lower the Tg of the coating

Linerless labels have made an appearance and an exit. Now, further examples of label/label constructions are appearing. Both involve silicone release coatings, and both have niche possibilities. Both neglect the fact that the release liner does more than just release the adhesive.

What about plastic replacing paper? Certainly, on the label side, significant shift has occurred. On the liner side, however, paper has made more progress in caliper control, flexibility and strength and environmental friendliness in recent years than plastic films have. The combination of cost and low stretch makes paper tough to beat in the roll label field.

One thing is likely – changes will be evolutionary, not revolutionary, just as they have been in the past.

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