# SILICONE ADDITION CURE EMULSIONS FOR PAPER RELEASE COATING

## Alain Fau - Andre Soldat
## Rhone Poulenc Chimie

## Biography

**ALAIN FAU**
Scientific and Technical Product Manager
Societe Rhone Poulenc Chimie
Lyons, France

Alain Fau is currently scientific and technical product manager in the Silicone Department of the Societe Rhone Poulenc Chimie of Lyons, France

Mr. Fau qualified as a chemical engineer at E.F.P. College, Lyons in 1960, the same year he joined the Societe Rhone Poulenc Chimie as an analyst. He later worked in production and research. Since 1975, he has specialized in research and development in paper coating silicones.

# SILICONE ADDITION CURE EMULSIONS
## FOR PAPER RELEASE COATING

Alain FAU  -  André SOLDAT

Rhone Poulenc Chimie

BP 22, 69191 St Fons Cedex, FRANCE

## ABSTRACT

The control of the reactions of Silicone addition cure systems has given rise to new developments in the field of paper coating, using solvent-based low temperature cure resins, and more particularly, solventless resins, which offer unmatched safety advantages.

More recently this technique was applied to emulsion systems. We will review the reaction control parameters and describe the emulsification process for these systems.

Existing achievements in terms of product performance and control of high dry content formulations now make the substitution of solvent based systems by emulsion based systems possible for the production of backings for pressure sensitive adhesive tapes and labels.

## INTRODUCTION

More than 20 years of research have been devoted to the concept of Silicone addition cure systems (using a platinum based catalyst) for paper release applications. However, it was not until the 1980's that this technique really began to develop after achieving better control over the problem of inhibition.

Because of their undisputed advantages over condensation cure systems, these new systems rapidly grew into a strong market position. Today, more than 70% of all paper and film coatings around the World, are performed with addition cure Silicones.

Some of the strong points of these new systems are : the very fast cure rate of the reaction at low temperature, the control of the reaction at normal temperature the non reversibility of the reaction and the resulting stable ageing performance, the control over the adjustable crosslinking performance which provides a means of producing coatings with the required hardness.

This method of controlling the stability of the reaction at normal temperature has been employed for the development of solventless resins.

The very fast cure rate of the reaction led to development of low temperature, solvent based resins which cure in 5 seconds at 110° C instead of 15 seconds at 150° C in the case of condensation cure resins.

The more recently produced emulsion based addition cure systems required to control their reaction in aqueous media. Some of the difficulties arising from this new development resided in :

- determining the choice of a cure system which would not be sensitive to water and emulsification.

- the necessity to protect the crosslinker, which is sensitive to hydrolysis reactions.

- the choice of a surface active system capable of providing a stable emulsion.

The first addition cure emulsions rapidly found a substantial outlet in the coating of food contact paper for bakery and pastry cooking. The subsequent optimization of the Silicone polymers used for this application resulted in the formulation of Silicone emulsions especially designed for the production of backings for pressure sensitive adhesive tapes and labels.


## 2    HEAT CURE TECHNOLOGY

### 2.1    Composition and function of the various system components.
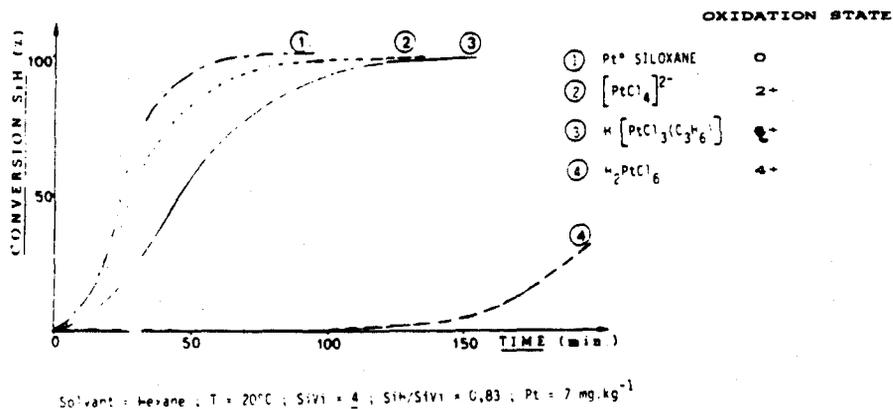
The reaction is obtained by combining the following elements :

The basic polymer  :   This consists of one or several dimethylpolysiloxanes which contain reactive vinyl groups. The position of these groups, their number, environment and accessibility will help to determine the reactivity of the system and the type of network obtained after cure, which constitutes the skeleton of the system.

A crosslinker  :  This is composed of one or several methylhydrogenopolysiloxanes. The position of the hydrogenous groups, their number, environment and accessibility will determine the minimum starting temperature of the reaction, its cure rate and anchorage performance on the substrate.

A catalyst  :   This is based on a platinum or Rhodium compound which is dispersed in a methylvinylsiloxane polymer.  The oxidation state of the metal, the nature of the binder and the content of platinum will determine the level of reactivity of the catalyst, and its shelf life stability.  Contents of 50 to 250 ppm of platinum per Silicone elastomer are used.  Figure I illustrates the significance of the degree of oxidation of the platinum on its reactivity. Platinum 0, which is the most reactive, is most frequently used.

FIGURE N° I
CATALYST
OXIDATION STATE OF THE METAL

Solvent : Hexane ; T = 20°C ; SiVi = 4 ; SiH/SiVi = 0,83 ; Pt = 7 mg.kg⁻¹

**A stabilizer** : Its function is to inhibit the reaction at room temperature, by forming a stable compound with the platinum. This will later be destabilized by Si H addition (2). The compromise between the stability of the cured system at room temperature and the crosslinking temperature threshold will be determined by the nature of the stabilizer and the concentration in which it is used.
Some of the products currently used are, among others :

- acetylenic alcohol (ethynylcyclohexanol) (3)
- acetylenic ketones (8-chloro, 1-octyne, 3-on) (4)
- diallkylmaleates (dimethyl maleate) (5)
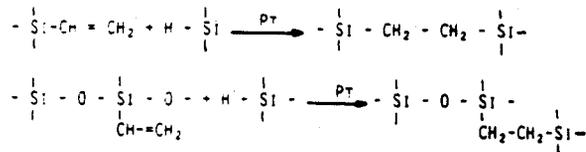- alkyl azodicarboxylates (ethyl azodicarboxylate) (6)


**A release controller** : This is a tri or tetrafunctional resin which contains vinyl or hydrogenous reactive groups. These products have less release than linear polymers, and thus enable the release performance to be adjusted.

The reactivity of these products must be tuned to the reactivity of the basic system, in order to integrate them into the network and thereby obtain a stable performance.

## 2.2 Study of the hydrosilylation reaction.

As shown on figure II, the basic reaction is simple. Contrary to condensation cure systems, it is a clear and non-reversible reaction.

FIGURE N° II

**BASIC REACTION**

$$-\overset{|}{\underset{|}{Si}}-CH=CH_2 + H -\overset{|}{\underset{|}{Si}} \xrightarrow{PT} -\overset{|}{\underset{|}{Si}} - CH_2 - CH_2 - \overset{|}{\underset{|}{Si}}-$$

$$-\overset{|}{\underset{|}{Si}} - O - \overset{|}{\underset{|}{Si}} - O - + H - \overset{|}{\underset{|}{Si}} - \xrightarrow{PT} - \overset{|}{\underset{|}{Si}} - O - \overset{|}{\underset{|}{Si}} -$$
$$\underset{CH=CH_2}{\phantom{xx}} \qquad\qquad \underset{CH_2-CH_2-\overset{|}{\underset{|}{Si}}-}{\phantom{xx}}$$

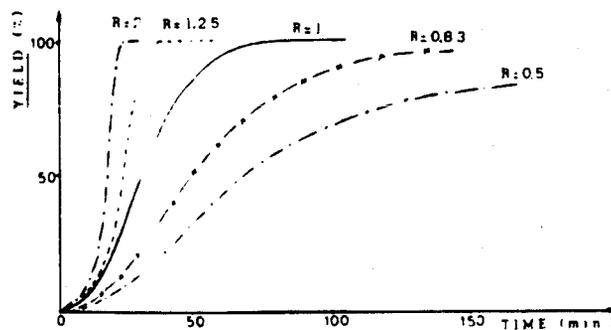Many factors enable us to control this reaction. As we have seen these include :

- the vinylsiloxane structure (basic polymer)
- the hydrogenosiloxane structure (crosslinker)
- the nature and ratio of the stabilizer
- the nature and ratio of the catalyst

In addition to these factors, two other parameters can be taken into account :
- the ratio of Si H/Si Vi active centers
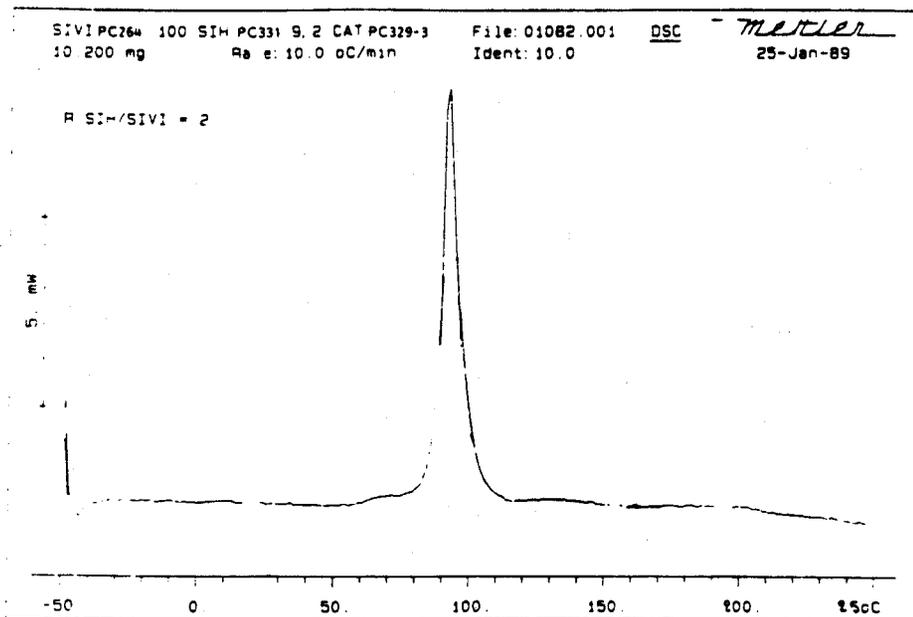- the reaction time and temperature.

Figure III shows the repercussion of an increased Si H/ Si Vi ratio upon the cure rate. The temperature threshold of the reaction is shown by the DSC graph in Fig IV

FIGURE N° III

CURE RATE AS A FUNCTION OF R

R = Si·H/Si·Vi

```
SIVI PC264  100 SIH PC331 9.2 CAT PC329-3    File: 01082.001   DSC    mettler
10 200 mg           Ra e: 10.0 oC/min         Ident: 10.0            25-Jan-89

   R SIH/SIVI = 2
```

By controlling these various parameters, the required reaction can be produced and the most suitable compromise for the application concerned can be obtained.
It is possible, for example, to observe the effect of a change in certain parameters on the performance ultimately obtained.

A densification of the network can be obtained <u>by increasing the ratio of active centers.</u> This hardens the coat and enhances its smoothness. The tighter cohesion thus obtained limits the variations in the release performance of the adhesived laminates. However, this also diminishes the release performance and elastomeric property of the coat.

<u>A higher crosslinker content</u> increases the SI H/Si Vi ratio, which accelarates the cure rate and improves enchorage onto the substrate.

<u>A higher catalyst content</u> accelerates the cure rate but increases the cost of the system. Beyond a certain threshold, it becomes necessary to reajust the stabilizer content in the system.

<u>An increased stabilizer content</u> improves the stability of the cured system. However, this requires a higher cure temperature threshold.

An attempt to optimize the cure rate may induce a reduction of the chemical interactionsof the silicone with the substrate (as in the case of a system with a low active center content) thus leading to a reduced anchorage to the substrate. Likewise, an improved cure rate can create an unbalanced Si H/Si Vi active center ratio which would increase the number of free active centers in the coating. This could result in side reactions with the adhesive, and poor storage stability.


## 2.3 Risk of inhibited reaction

The amount of risk is important. For a long time it has been a major obstacle to the development of these systems.

. The greatest risk concerns the inhibition of the platinum catalyst. Inhibors of this catalyst include :

- Amines, which may be present through several media (paper tackifiers,    EDTA laminating agents, antislip agents on certain polyethylene films, insolubilizing agents, dyes contained in the paper...)

- Sulphurous organic derivatives. These are often present in the basic paper, antifoaming agents, surface active agents...

- Many metals in the form of organic salts, such as tin salts (used in condensation systems), zinc, chromium, iron and lead salts...

These products have a direct influence on the platinum compound either by replacing the platinum contained in the compound, the inactive platinum then being precipitated in a colloidal form, or by forming a more thermally stable compound which can no longer be used within the temperature range currently applied in paper manufacturing. The slightest trace of these products will therefore have noxious effects in these applications.

. A second type of risk, although they less frequently occur, concerns an eventually unbalanced active center ratio. The unsaturated products may produce double bonds which will hinder the action of the vinyl groups and slow down the reaction. Oxidizing products (which are often present in bleached paper, can lead to a consumption of Si H groups which would equally slow down the cure rate.

Today, these various risks are better known, particularly to paper manufacturers and they no longer constitute a major obstacle against the utilization of these systems.


## 3    SILICONE ADDITION CURE EMULSIONS

Three main forms of silicone addition cure systems are used :

- Solvent based dispersions are the oldest, most widely used form. Their application is both simple and highly flexible. However, in view of the risks involved in solvents, users have become increasingly reluctant to the utilization of these systems.

- More recently, solventless systems have developed very rapidly. Today, they represent almost 40% of the world market. These systems are based on very low molecular weight polymers, which can only be applied to very high grade paper in terms of pore sealing and smoothness of the surface. In addition to which, special coating equipment is required.

- Emulsions systems now offer an alternative to solvent based systems. They do not require any special equipment and can often be applied to lower grade substrates.

## 3.1 Manufacturing technique

An emulsion can be defined as a fine dispersion of a liquid into another liqui . The two fluids are neither miscible nor soluble into one another. The mixture is stabilized by one or several surface active agents.

The dispersion under present consideration is oil in water. The resulting emulsion can then be further diluted in water. Solvents are no longer necessary. There are two ways of obtaining Silicone addition cure emulsions :
- By incorporating polymers directly into an emulsion,
- by polymerization of monomers after incorporating them in an emulsion.

The first technique requires low molecular weight polymers. On the other hand, the second technique produces high molecular weight polymers while a low viscosity is still maintained in the emulsion.

At present, the first technique is preferred. It offers a more reliable way of obtaining an even polymer skeleton and a good spread of residual active centers, without risks of interfering chemical functions. The systems remain stable after cure and the risk of penetration into the substrate can be compensated by a high cure rate.

## 3.2 Choosing the surface active system

This is one of the key factors for a performant product.

- Low molecular weight silicone fluids (low viscosity) being totally unsuitable for emulsification, the first function of the surface active agent is to produce a thick, even, aqueous phase after it has been mixed with the polymers, capable of transferring energy which will facilitate the grinding of the emulsion.

- It is important to use an ionic surface-active agent. Cataionic systems are not suitable with Silicones, and can produce substantive emulsions, which are not the intended purpose for coating applications. Non ionic systems are preferred. They make the emulsions highly compatible with the polymeric additives used in the formulation.

- The stabilizing power of the surface active agents on the emulsion must be very high in order to be effective in the small proportion in which they should be used. This is due to the fact that they release agents and as such, can have

a noxious effect on the ultimate release performance.

- To avoid all risks of migration, the surface active agent must include active centers capable of reacting with those of the Silicone, to form an integral part of the network after cure.

- The surface active agent must have great affinity with the substrate (paper). For a good wetting performance, its surface tension must be sufficiently low.
- Active centers capable of reacting with those of the paper and acting as anchorage primer, can also be incorporated.

- Thesurface active agent must present a good film forming capacity in order to have a pore sealing effect on the paper surface.

- The possible chemical reactions of the surface active agent with the Silicone polymers must be controlled. Hence, to obtain a good stability of the system and avoid all premature reaction, surface active agents of different nature can be used for the polymer, the crosslinker and the catalyst (7).

- The surface active agent must be capable of providing a water retention property to the system, equal to that of the paper, in order to form a balanced coating of all the constituents included in the formulation (no substantivity).

- The choice of the surface active agent molecular weight enables us to control the particle size. A low molecular weight will result in very fine particles, of the order of 0.2 to 0.3 microns. On the other hand, a high molecular weight (as in the case of protective colloids), will produce much coarser particles of 2 to 3 microns. These large particles are preferred for two reasons :
    - to limit the penetration into the substrate
    - to obtain a good compromise between a sufficiently stable emulsion in a diluted form, in order to resist the shear strenght of the coating head, and avoiding a premature destabilization of the concentrated emulsion during the drying stage.


## 3.3   The emulsion catalyst

The selected catalyst must not be sensitive to water. Platinum based, chlorine free compounds with zero degree oxidation are generally chosen. It is also important to make sure that the surface active agent used to stabilize the emulsion will not inhibit the Si H/Si Vi crosslinking reaction.


## 3.4   Presentation of the system

The systems can be presented under various forms : either in the form of separate contituents, which provides great flexibility in the formulation, or in the form of matching constituents which are easier to use. A convenient presentation, in the form of 3 components is often proposed:

Compound A contains the Silicone polymer, the crosslinker and the reaction stabilizer.
Compound B contains the release controller and the crosslinker,

Coumpound C includes the platinum catalyst which matches the basic polymer.

Each component of the commercial product is adjusted to a 40% concentration.

# 4 PROCESSING OF EMULSION BASED SYSTEMS

For a long time, the use of emulsion type has been limited to applications other than backings for adhesives (P.S.A. type). These applications included food packaging, laminate separators, transfer paper for synthetic rubber and release substrates for asphalt or uncured rubber.

The difficulties involved were connected with the necessity to use overdiluted formulations (5 to 10%) to maintain sufficient stability in the coating baths. This high dilution, together with a slow cure rate led to a water saturation of the substrates, hence to problems of size stability and curling. The penetration of the silicone into the substrate had to be limited by combining soluble and film forming organic polymers with the silicone, in order to produce a reaction both on the paper and on the silicone. The resulting increase in viscosity and pore sealing effect tended to reduce the penetration of Silicone into the paper. However, these products also altered the ultimate release performance. And finally, large quantities of water had to be eliminated from the paper, which strongly hindered productivity.

The control of addition cure emulsions enabled stable systems with high dry content formulations (20 to 25%) to be developed. The viscosity of such formulations remains low ( < 50 mm2/sec) and the fast cure rate prevents the penetration of the silicone into the paper.

## 4.1 Coating conditions

- The coating of emulsion systems is performed with conventional coating heads. The use of high dry content formulations requires very low wet deposits. Coating equipment, of the Meyer bar or air knife type are not suitable for this application. The development of an engraved ceramic roll has given very promissing results. The very high degree of hardness of this material enables rolls with very fine engravings to be produced, and also makes the differential speed coating technique now possible. Good coating quality has been achieved with wet coatings of 4 to 5 g/m2.

The preparation of the high dry content coating formulation requires a great deal of attention. The following parameters must be carefully observed:

- order of incorporation of the constituents
- poor rate
- agitation efficiency
- agitation time before each constituent is added, particularly the catalyst.

Generally, this operation can be completed within 20 minutes.

EXAMPLE OF FORMULATION (ORDER OF INCORPORATION)

| | | | | |
|---|---|---|---|---|
| (1) | 30 parts | - | Component A | = Polymer + crosslinker + stabilizer |
| (2) | 30 " | - | Component B | = Release control agent |
| (3) | 36 " | | Condensation water | |
| (4) | 1 " | - | Any other additive | = antifoam, surface active agent, film forming agent.... |
| (5) | 3 " | - | Component C | = Polymer + catalyst |

The characteristics of the above formulation are :

| | |
|---|---|
| Dry Silicone content | = 25% |
| Surface tension | = 35mM:m |
| Viscosity (25°C) | ≃ 40 mm2/sec |
| Bath stability (25° C) | ≃ 4 hours |
| pH | ≃ 6 |

Using a dry Silicone content of 1g/m2 as a reference, the total wet deposit must be 4g/m2 (i.e. 3g of water). The calory consumption to evaporate 3 grammes of water, is the equivalent of that needed for 7 grammes of solvent (quantity generally observed in solvent based resin coatings). At a given cure temperature, the coating rate of an aqueous system (25% dry content) is the same as that of a solvent based system (12.5% dry content).

4.2    The coating mechanism is complex. The emulsified system is applied to the surface of the paper. The large particle size prevents an excessive penetration into the paper. The coating is rapidly heated in the tunnel dryer. The elimination of water, combined with the thermal shock, rapidly leads to a destabilization of the emulsion system. Those surface active agents which present a high degree of affinity with the paper migrate rapidly towards its surface while the less organocompatible Silicone remains on the outer face of the layer. An infrared examination (ATR) shows this selective transfer. On the paper surface, the surface active agent acts as a surface sealing agent and anchorage primer. Its water retention power will slow down the penetration of water into the substrate. After the constituents have been released, curing must follow very quickly to block the Silicone in its solid state on the surface of the paper. This mechanism requires a temperature of approximately 100°C on the paper surface. Although the cure temperature is lower than 100°C, the separation of the constituents after destabilization of the emulsion system will only be complete at a temperature above or equal to 100°C.
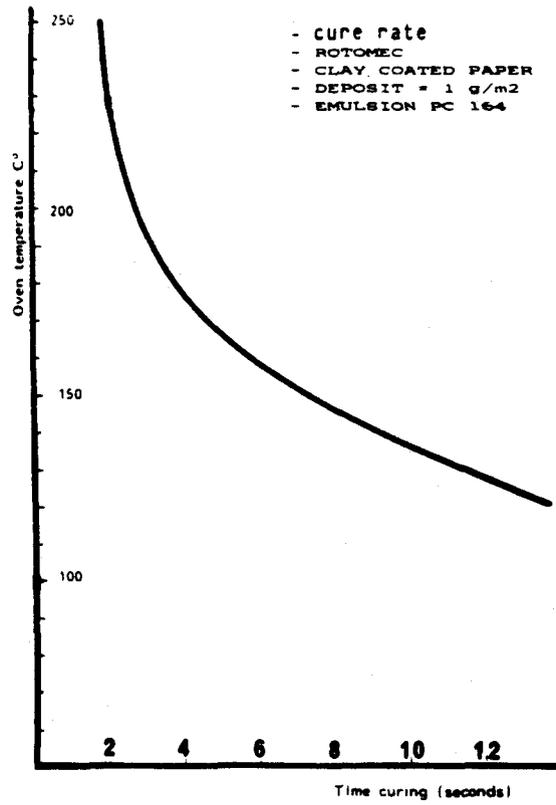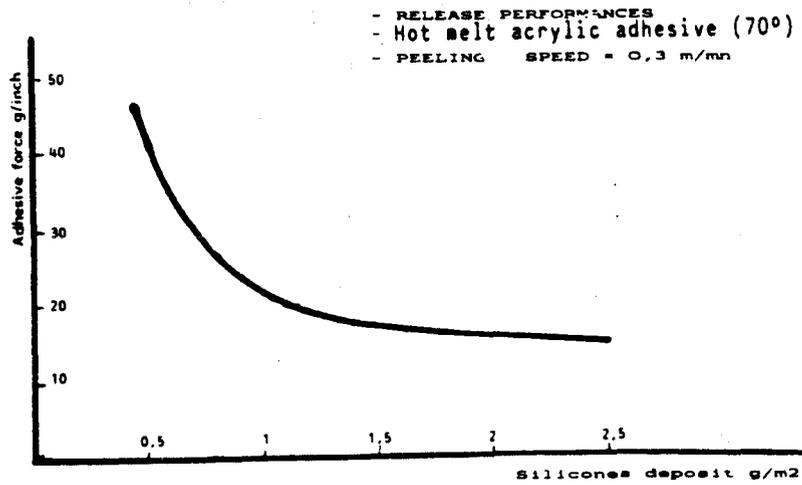
10

FIGURE N° V

- cure rate
- ROTOMEC
- CLAY COATED PAPER
- DEPOSIT = 1 g/m2
- EMULSION PC 164

Oven temperature C°

Time curing (seconds)



FIGURE N° VI

- RELEASE PERFORMANCES
- Hot melt acrylic adhesive (70°)
- PEELING    SPEED = 0,3 m/mn

Adhesive force g/inch

Silicones deposit g/m2

11

4.3   As regards <u>the penetration of the Silicone</u> into the paper, if we compare solvent based, solventless and aqueous systems, we observe that the size of the molecules used in each case, varies considerably.

In the case of solvent based resins, the molecules have a high molecular weight of about 500 angströms in size. The size of the paper pores is generally larger.   This implies that the paper used must be previously pore-sealed with a polymeric coating.

With solventless systems, this aspect is even more critical. The size of the molecules is about 50 to 100 Angströms.   Consequently, the pore sealing treatment is even more crucial. A direct application of a 1 micron coating of Silicone could only be made on the more expensive paper with a high quality surface finish.   However, in the case of emulsions, the particle size is of the order of 20 000 to 30 000 Angströms. This size is much more suitable for any paper surface.   Less elaborate, and therefore less expensive paper will often be sufficient for this application.


5   <u>PROPERTIES AND PERFORMANCE OF ADDITION CURE EMULSIONS</u>

5.1 <u>Coating cure rate</u> .

This has been tested on  an industrial coating machine, using 65g/m2 clay coated paper.   The dry Silicone content coating was set on 1g/m2. The selected Silicone emulsion is a medium range product (PC 164) with an average vinyl content.   Figure V shows the time taken at different temperature levels inside the tunnel dryer, for total cure (subsequent adhesivation equivalent to 100%). It was observed, for example, that on a machine equipped with a 16 meter long tunnel dryer operating at 200/220°C, complete cure could be achieved at a coating rate of 400 m/minute.


5.2 <u>Dry Silicone coatings</u>

Coatings must be adjusted to suit the quality of the basic paper used and the required release performance. Figure VI shows the influence of the coating on the release performance, using clay coated paper and an acrylic adhesive.

5.3 <u>Release performance</u>

The release performance was tested at different peeling rates. The FINAT test conditions were observed (20 hours at 20°C under a 70g/cm2 pressure). The performance achieved with a SBR adhesive are very good compared with those of a solvent based resin.   The performance obtained with a solventless resin is substantially better.   Figure VII shows these results. When in-line adhesivation is operated, the adhesive force increases slightly during the first week and then becomes stable (Figure VIII).

**12**

FIGURE N° VII

- RELEASE PERFORMANCE
- SBR adhesive (20°C)
- DEPOSIT 1 g/m2
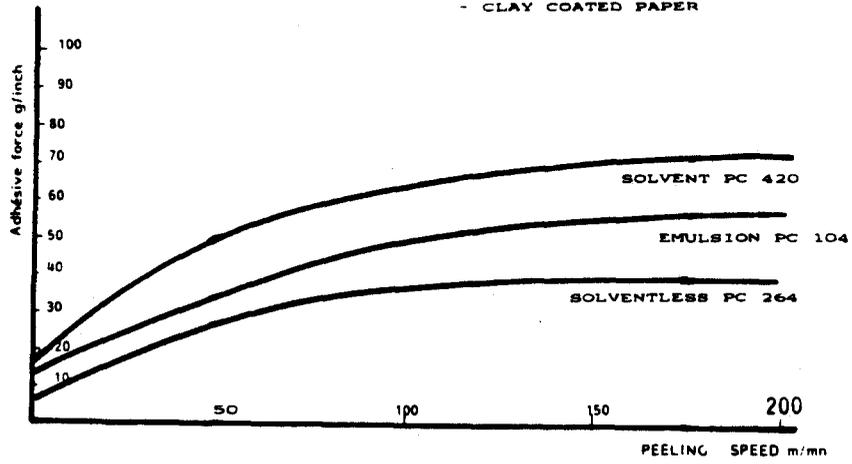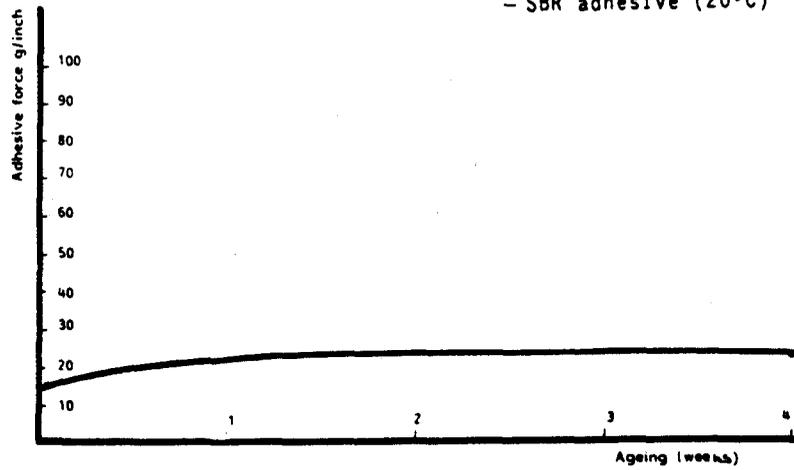- CLAY COATED PAPER



FIGURE N° VIII

- RELEASE PERFORMANCE
  " AGEING "
- SBR adhesive (20°C)



13

## CONCLUSION

The control of heat cure emulsion techniques has opened the way to substantial progress in paper coating techniques. The systems now developed have given rise to stable high dry content, low viscosity, bath formulations. These systems present a very fast cure rate. Their performance can be adjusted according to the basic polymer used. The level of performance achieved is at least equal to that of solvent based systems.

The substitution of solvent based systems by solventless systems has become possible, and is now finding its place in the production of backing papers for pressure sensitive adhesives.

## BIBLIOGRAPHY

Dr. J. CAVEZZAN (Rhône Poulenc)
"Investigation of the factors controlling the rate of hydrosilylation of unsaturated compounds" - Commounication held at VIIth International Symposium on Organosilicon Chemistry, KYOTO, JAPAN September 9.14.1984

Dr. R.P. ECKBERG (General Electric Company)
"Inhibition of solventless silicone paper release coatings"
High solids coatings 18 1983 Buyer's guide issue.

G.V. KOOKOOTSEDES and al. US. 3.445.420
(5/20/69 to Dow Corning)

J. CAVEZZAN            US 4.595.739
(6/17/86 to Rhone Poulenc)

R.P. ECKBERG            US 4.256.870
(3/17/81 to General Electric)

J. CAVEZZAN            US 4.640.939
(2/3/87 to Rhône Poulenc)

A. FAU            US 4.791.029
12/13/88 to Rhône Poulenc)