

# **ADHESION 9**

**Edited by  
K. W. ALLEN**

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# ADHESION 9



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Edited by

K. W. ALLEN

*Adhesion Science Group, Department of Chemistry,  
The City University, London, UK*



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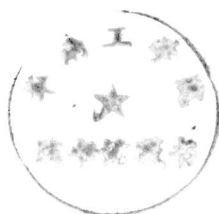
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## ADHESION 9



*This volume is based on papers presented at the 22nd annual conference  
on Adhesion and Adhesives held at The City University, London*

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## Preface

The use of adhesives continues to increase both in importance and in areas of use, particularly in engineering construction. Alongside this is a steady growth in our fundamental understanding of the factors involved. Both of these topics are reflected in various meetings and nowhere more consistently than at the Annual Conference on Adhesion and Adhesives at The City University each Easter. 1984 was the twenty-second of these when, once again, people came from far and near to present accounts of their work and to discuss them in all their variety. This publication makes the papers available to the wider audience who were not able to attend in person.

In presenting this volume, may I express sincere gratitude, both personally and on behalf of the University, to all those who contributed in so many and various ways to the conference.

K. W. ALLEN

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# Chapter 1

## TEXTILE-to-RUBBER ADHESION:

### THEORY and PRACTICE

David B. WOOTTON

MILLIKEN INDUSTRIALS Ltd., BURY, LANCs.

#### 1. INTRODUCTION

The reinforcement of rubber with textiles plays a very important part in the modern world; it is only necessary to consider the role of the tyre in present day communication and transport to appreciate this. However, the full performance of these composites can only be realised if the adhesion between the various components is adequate.

In the earlier days, when cotton was the major reinforcing fibre, adhesion levels - and performance - were lower: the adhesion obtained between the textile and the rubber was mechanical, arising from the embedding of the fibre ends into the rubber matrix. With the advent of the artificial or man-made fibres, these, being continuous filament yarns, do not shew any significant mechanical adhesion, so that some form of adhesive treatment is required in order to achieve the necessary levels of bonding to give the full reinforcing effect.

#### 2. GENERAL REVIEW OF SYSTEMS

There are four main types of fibre used in the manufacture of the reinforcing fabrics. These are:-

RAYON: regenerated cellulose

POLYAMIDE: nylons 6.6 and 6,

POLYESTER: poly (ethylene terephthalate),

ARAMID: poly (para-phenylene terephthalamide).

The first of these, rayon, requires a treatment with an adhesive comprising a mixture of a resin with rubber latex. Originally, the resin was casein based, but in 1935, DuPont chemists developed a new system using a resorcinol/formaldehyde resin. This system, a typical formulation of which is given in Table 1, is applied to the fabric, the excess removed, the water dried off and the resultant dip film baked to develop the full adhesive characteristics. A similar resin/latex (RFL) dip system is used for nylon. There are some differences for the optimum results with nylon, but these will be considered in more detail later.

TABLE 1:

BASIC RFL FORMULATION

	PARTS BY WEIGHT	
	DRY	WET
WATER	-	257.8
RESORCINOL	9.4	9.4
FORMALDEHYDE (37% soln.)	5.1	13.8
CAUSTIC SODA (10% soln.)	0.7	7.0
LATEX (40% solids)	84.8	212.0
	<hr/> 100.0	<hr/> 500.0

With polyester, however, these systems do not give adequate adhesion and a pre-treatment is required in order to obtain good adhesion. There are three main types of treatment used with polyester. The first of these is a pre-treatment applied at the spinning stage; various materials have been used but the most important in use at present are epoxy-derived products. An aqueous solution of the epoxy is applied to the yarn just after spinning and a heat treatment given to modify the surface properties of the yarn. After this pre-treatment, a standard RFL is used on the textile construction, applied in much the same manner as for rayon or nylon. The second group of systems use a pre-treatment

applied to the textile structure after the assembly process, again followed with an RFL. iso-Cyanate solvent solutions were the first of this type of treatment, but in view of the hazards of such materials are not much used these days; however, a modification of the simple iso-cyanate, the 'blocked' derivative, is used in an aqueous system, again developed by DuPont, known as the 'Shoaf' or D 417 dip. The third range of polyester treatments are modified RFL systems. Basically, the resin component of the dip is modified, to increase the compatibility with the fibre. One of these systems modifies the resin by using a proportion of an aromatic or alicyclic aldehyde, as partial replacement of the formaldehyde, but the most important of these, developed by I.C.I., incorporates a resin containing a proportion of ortho-chlorophenol.

TABLE 2:

## RFL MIXING SCHEDULE

	PARTS BY WEIGHT	
	WET	DRY
WATER	121.8	-
RESORCINOL	9.4	9.4
FORMALDEHYDE (37% soln)	13.8	5.1
CAUSTIC SODA (10% soln)	7.0	0.7
	152.0	15.2
LATEX (40% solids)	212.0	84.8
WATER	136.0	-
RESIN SOLUTION	152.0	15.2
	500.0	100.0
TOTAL SOLIDS CONTENT:	20.0%	
RUBBER TO RESIN RATIO:	5.5 :1	
FORMALDEHYDE TO RESORCINOL (MOLAR)	2 :1	

In a similar way, a pre-treatment is necessary with aramid. Here, a some-what simpler pre-treatment is used, based on an epoxy, followed with an RFL.

It can be seen therefore, that all the textile bonding systems use systems employing an RFL dip, or a modification thereof, so these will be considered in rather more detail.

### 3. THE R.F.L. SYSTEM

The basic mixing schedule for an R.F.L. dip is shewn in Table 2. This is essentially the same formulation given before, but indicates the order of mixing of the various ingredients. Firstly, the resorcinol is dissolved in water, the formaldehyde added and caustic soda as the catalyst. The resulting resin solution is then added to the diluted latex. This is the basic system; however, there are many aspects of this apparently simple system which have significant effects on the properties of the resultant adhesive.

#### 3.1. THE R.F. RESIN

Firstly, there can be considerable variations in the ratios of the reactants in the resin condensation. The essential chemistry of this condensation is given in Figure 1. The first stage of the reaction is a methylation of the resorcinol, in the '2' position: this then reacts rapidly with another molecule of resorcinol, giving a dimer. The reaction proceeds in this way, leading to an oligomer generally straight chains of up to about 6 units. After this stage, more complex crosslinking occurs, yielding the final resin product.

The degree of this crosslinking can, of course, be modified by the molar ratios of formaldehyde to resorcinol. Theoretically, a molar ratio of 2:1 should result in a fully crosslinked resin, but generally, in an RFL adhesive, a slightly higher ratio, even perhaps up to 3:1 is used. Surprisingly, however, quite wide variation in this ratio has relatively little effect on the final adhesion obtained with the dip.

Another factor, which does affect the final adhesion is the pH at which the condensation occurs: this is controlled by the addition of alkali (usually sodium hydroxide). This effect can be seen in Fig 2: as the pH, at which the

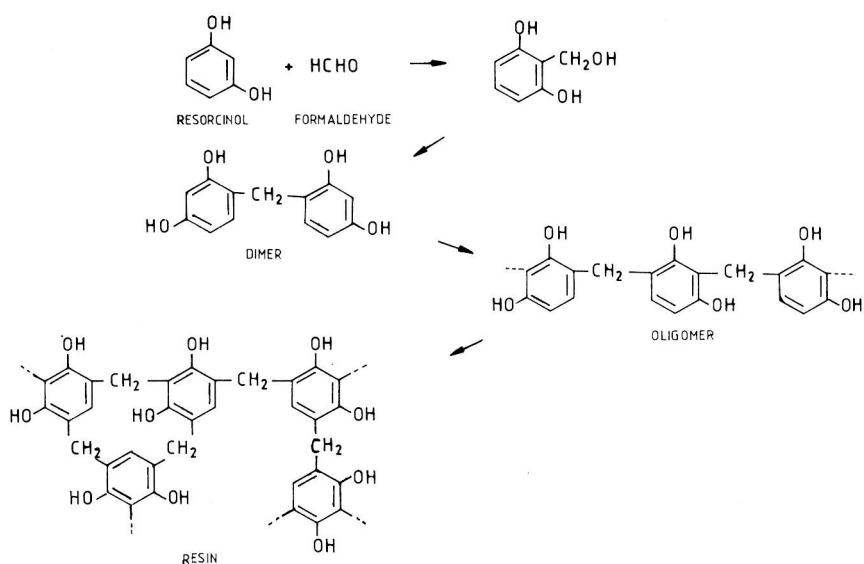


FIGURE 1: CONDENSATION of RESORCINOL with FORMALDEHYDE.

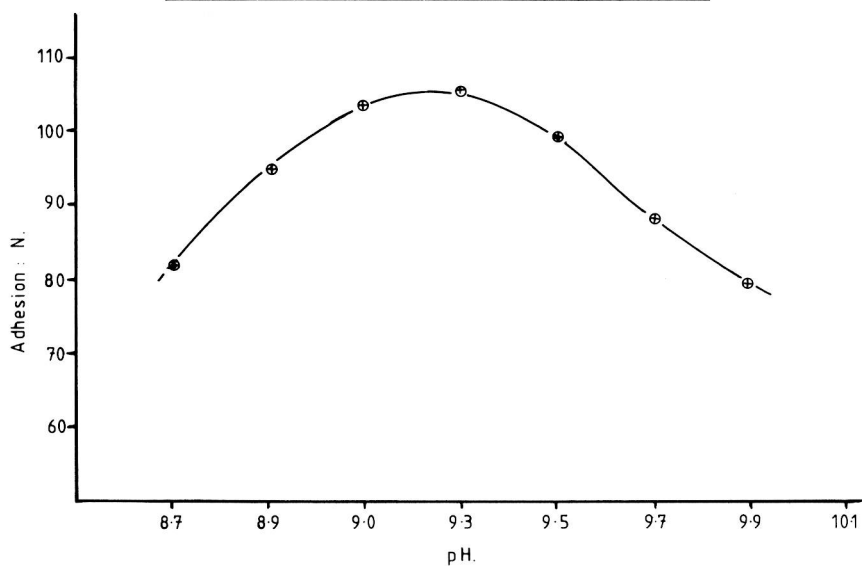


Figure 2 : Effect of pH on Adhesion.

dip was prepared, is increased, so the adhesion increases, to an optimum at around pH 9.3, beyond which the adhesion level falls. This optimum pH can vary slightly, depending not only on the actual dip formulation but also on the rubber compound to which the textile is to be bonded, but for most practical applications the exact matching of dip to rubber is of debatable worth, except perhaps where just one fibre type and one compound only are in use.

Earlier, it was stated that the resin solution was added to the latex. Again this simple statement covers various significant effects. In the early days of RFL, when the latex used was ammonia stabilised natural latex, it was essential that the resin be allowed to condense to a reasonably advanced stage before addition to the latex, otherwise the formaldehyde would react preferentially with the ammonia, which both prevents the resin condensation and destabilises the latex. With the advent of the synthetic latices, however, it was found that the resin could be allowed to condense in the presence of the latex. Although the chemical nature of the resultant dips are not significantly different, certain differences in the morphology of the dips and in their behaviour became apparent.

When the resin is allowed to condense in the presence of the latex, the oligomer formed in the earlier stages of the condensation exhibits certain surfactant properties and will displace some of the stabilising soap molecules from around the rubber particles in the latex; this of course leads to a much more intimate dispersion of the resin in the rubber - the two not being thermodynamically compatible and therefore existing in separate phases - as the further crosslinking of the resin leads almost to encapsulation of the rubber particles with the resin, whereas the precondensed resin, already in larger complex molecules, tends to remain as a discrete separate phase.

The main technological differences between the two systems concern the ageing and curing characteristics. In Fig 3 the effects of ageing, timed from the addition of the resin to the latex, on the adhesion, achieved with dips prepared by the two methods, is shown. Up to about 24 hours ageing (this is the usual "maturation" period allowed in preparation of the dips) the two stage mix, i.e. with the resin condensed before addition to the latex, gives slightly higher adhesion: this is to be expected as the resin, already formed by this method, is the main contributor to adhesion with the textile. After this maturation period,

both dips give very similar levels of adhesion, but with the two stage mix, the adhesion tends to fall after about four days, and at least 25% of the optimum adhesion is lost after 14 days, whereas with the single stage mix, there is less than half this loss in adhesion after 42 days storage of the dip.

The other major differences arising from the method of mixing concerns the optimum curing (or baking) conditions for the dip. The cure characteristics of the two systems are shown in Fig. 4. It can be seen that with the two stage mix, the optimum adhesion is obtained with a baking exposure of around 105 seconds at 150-160°C, whereas the single stage mix gives optimum results with a much shorter exposure at much higher temperatures (around 70 seconds at 205°C)

### 3.2 THE LATEX COMPONENT

Of course, the resin is only one half of the dip, the latex being the other. Originally, the only latex available was natural, but this was replaced with SBR latex. This worked perfectly satisfactorily with rayon, but still left something to be desired with nylon. This was overcome by the development of a terpolymer latex of styrene, butadiene and 2 - vinyl pyridine. (Generally referred to as VP latex). The replacement of SBR latex with VP latex has a marked effect on the adhesion obtained with nylon, as shown in Fig. 5. As can be seen, the replacement of around 50% of the SBR with VP gives a very significant increase in adhesion, and further increases are obtained with up to 80% VP. Above this level, there is only a modest increase, but for many applications, it is considered preferable to use 100% VP, to ensure that optimum adhesion is reproducibly obtained.

## 4. RUBBER COMPOUNDING EFFECTS

This covers the major variables and their effects on the performance of RFL systems: this of course represents only one side of the total bond system, the rubber compound being the other side. There are many more variables in rubber compounding, which can have significant effects on the resultant adhesion.

### 4.1 POLYMER AND FILLER EFFECTS

The first of these is the polymer. Excluding the speciality elastomers, of the general purpose polymers, SBR generally gives the highest measured adhesion,

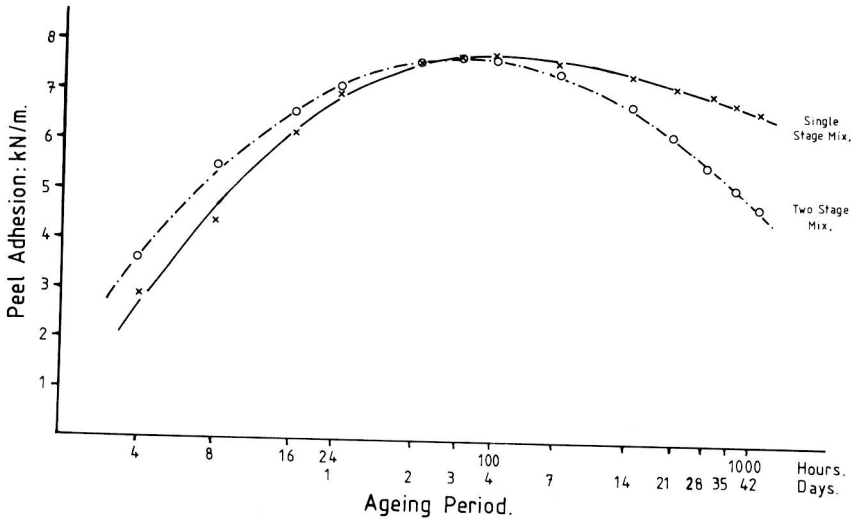


Figure 3: Effects of Ageing on RFL Dips.

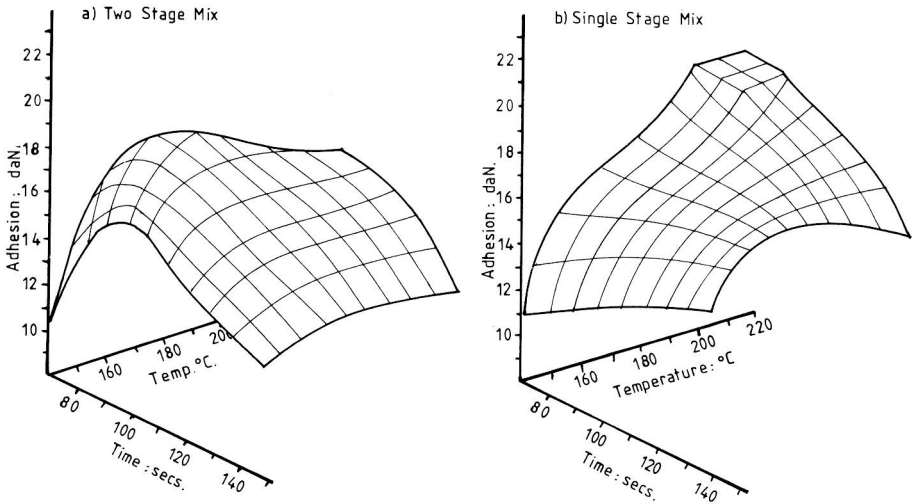


Figure 4: Cure Characteristics of RFL Dips.



with the level dropping as the proportion of natural rubber increases. Secondly, the filler used can have some effects: there are considerable differences in the adhesions obtained between the main classes of fillers, such as the mineral fillers and carbon blacks, but within the different classes, there are not very great differences.

However, for most applications, the polymer/filler system is usually dictated by the properties necessary to meet the service requirements, so that the main variations can only be made in the vulcanizing system.

#### 4.2. THE CHOICE OF CURING SYSTEM

In Table 3 are shown the adhesion levels obtained with various curing systems. From this it is readily apparent that low sulphur or sulphurless systems do not give good adhesion. In the more conventional systems, those with a slower rate of cure generally give the better adhesions and, where faster cures are required, amine activation of thiazoles (either separately, as with DPG, or "internally" with the sulphenamides) give better adhesions than thiuram or dithiocarbamate activation.

Nevertheless, even though the curing systems chosen gives good adhesion, the actual level of adhesion is still affected by the state of cure achieved in the final composite. Fig. 6 shows these effects. It can be seen that the optimum adhesion is obtained somewhat after the point generally considered to be optimum cure, from the conventional assessment of development of physical properties: however, the adhesion levels tend to drop quite rapidly on continuing cure beyond this optimum level. Comparing this effect of cure time with the development of physical properties, it would appear that the cure for adhesion follows more closely the development of modulus and resilience rather than tear strength, as might have been expected when considering the failure with a peel adhesion test. This suggests, perhaps, that the restriction of deformation at the failure interface, due to the stiffer, higher modulus compound, is more important in achieving high adhesion than are high tear strength or ultimate tensile strength.