

## CHAPTER V

### RAW MATERIALS

Raw materials for manufacturing Neoprene adhesives consist of the followings:-

#### Function

- 5.1 Neoprene : Body of adhesive
- 5.2 Resin : Tackifier rubber will not stick to any other materials without tackifier.
- 5.3 Oxide : - Act as the crosslink of resin and rubber, activate the formation of strong band by reacting with resin,  
- acid acceptor
- 5.4 Solvent : Dissolve solid materials Viscosity and drying time adjuster

## 5.1 Neoprenes

The polymer structure of commercial neoprene is determined by the manner in which the chloroprene monomer, 2-chloro-1, 3-butadiene, reacts with the growing polymer chain. Upon polymerization, the chloroprene moiety may take any of four isomeric forms, as shown in Table 5.1. The proportions of these configurations determine the amount of crystallization (trans-1, 4) and reactivity towards vulcanization (1, 2 addition).

Rapid bond strength development of neoprene contact adhesives is associated with crystallization resulting from a very high level of trans configuration in which there are no side groups bulkier than the chlorine atom. Neoprene type W, a noncrystallizing polychloroprene, contains 85 % trans-1, 4 segments, whereas neoprene type AC, a fast-crystallizing polychloroprene, contains about 90 % trans-1, 4.

The principal neoprene types used in adhesives are summarized in Table 5.2 along with appropriate physical properties.

Presently, two manufacturing processes are used to prepare chloroprene monomer: the acetylene route and the butadiene route. Recently, the latter has come into favor as a result of the increasing cost of acetylene.

Neoprenes AC and AD are the main types of polychloroprene used in adhesives. The former is more popular in the U.S., the

Table 5.1 Molecular structure of Neoprene.

Type of Addition	Formula	Comments
Trans-1,4	$  \begin{array}{c}  \text{H} \quad \text{H} \\  \diagdown \quad \diagup \\  \text{C} \quad \text{C} \\    \quad \quad   \\  \text{H} \quad \quad \text{C} \\  \quad \quad   \\  \quad \quad \text{Cl}  \end{array}  $	increases crystallization
Cis-1,4	$  \begin{array}{c}  \text{H} \quad \quad \text{H} \\  \text{C} \quad \quad \text{C} \\    \quad \quad   \\  \text{H} \quad \quad \text{C} \\  \quad \quad   \\  \quad \quad \text{Cl}  \end{array}  $	decreases crystallization
1,2	$  \begin{array}{c}  \text{H} \quad \text{Cl} \\  \diagdown \quad \diagup \\  \text{C} - \text{C} \\    \quad   \\  \text{H} \quad \text{CH} \\  \quad \quad    \\  \quad \quad \text{HCH}  \end{array}  $	active sites for vulcanization (decreases crystallization)
3,4	$  \begin{array}{c}  \text{H} \quad \text{H} \\  \diagdown \quad \diagup \\  \text{C} - \text{C} \\    \quad   \\  \text{H} \quad \text{C} - \text{Cl} \\  \quad \quad   \\  \quad \quad \text{HCH}  \end{array}  $	decreases crystallization

Table 5.2 Properties of Neoprene Types Used in Solvent Adhesives.

Type of Neoprene	Characteristics	Specific gravity	Rate of crystallization <sup>a</sup>		Viscosity Polymer <sup>b</sup>	Soln <sup>c</sup>	Stability <sup>d</sup>
W	General purpose elastomer, good tack, lower cohesive strength	1.23	30 hr		45-55	20-28	+2%
AC	General purpose, quick setting adhesive elastomer, good stability and cohesive strength	1.23	2 1/2 hr	soft	75-90	45-65	
				med.	91-105	65-90	-37%
				hard	106-120	91-160	
AD	Similar to AC with better color and viscosity stability	1.23	2 1/2 hr	AD10	70-80	40-50	
				AD20	81-95	50-80	+28%
				AD30	96-113	80-120	
AF	Very slow-crystalizing, R.T-curing adhesive elastomer. Rapid strength development with good strength at elevated temperatures	1.23	400 hr		45-55	•	-17% (then increase after 8 hours)
AG	Gel elastomer-improved application properties, particularly at high solids	1.23	does not crystallize		90	•	fair

Table 5.2 (cond't)

Type of Neoprene	Characteristics	Specific gravity	Rate of crystallization <sup>a</sup>	Viscosity Polymer <sup>b</sup> Soln <sup>c</sup>	Stability <sup>d</sup>
AH	Noncrystallizing, peptizable, dispersible polymer exhibiting good application characteristics	1.23	does not crystallize		

\* Miling required for smooth solution.

a Time to reach a room temperature Shore A hardness of 60 after being heated 30 min at 158°F

b Mooney viscosity M.L. - 212°F (1 + 2½ min reading).

c Viscosity of 5% solids solution in xylene - unmiled rubber, cps.

d % Mooney viscosity change of raw material after 12 months storage at 100° F unless otherwise noted.

latter in Europe and Japan. Adhesives prepared from these two types perform equivalently. They are characterized by rapid cohesive strength development, good heat-resistance and application properties, and when properly formulated yield nonphading cements.

Neoprene AD is lighter in color in both chip and solution, more resistant to discoloration from contamination with trace metals such as iron, copper, etc., cures faster with NA-22 (ethylene thiourea) but slower with metal oxides (therefor, also less scorchy), and is less resistant to discoloration from UV light than Neoprene AC.

Most adhesive manufacturers prefer the lower Mooney viscosity types of Neoprene AC and AD (e.g., AD 10 and AC soft-see Table). Lower Mooney viscosity grades require little or no mechanical breakdown and dissolve faster, resulting in less "stringy," lower viscosity, higher solids, and longer tack range cements. However, lower Mooney grades have lower Mooney grades have lower cohesive strength.

### Neoprene AF

Adhesives based on Neoprene AF, a carboxyl-containing polychloroprene, are characterized by faster cohesive strength development at room temperature higher strength at room elevated temperatures, increased resistance to phasing, but are poorer in stability compared to the rapidly crystallizing Neoprenes AC and AD.

These characteristics are the result of interaction of the polymer with metal oxides rather than crystallization. The crystallization rate of neoprene AF is much slower than that of Neoprene AC or AD, and plays no significant part in the development of bond strength in adhesive films. Unlike other room-temperature-curing adhesives, Neoprene AF can be compounded to provide solutions stable for months.

In compounding Neoprene AF adhesives, their interaction with metal oxides must be considered. Variables such as resin type, solvents water, heat history, and even order of addition are also very important. The most useful stabilizers for Neoprene AF are the tertiary butyl phenolic resins, which contribute significantly to the improved hot strength in adhesives based on other neoprenes. Hot strength in Neoprene AF is much less dependent on resin concentration than in other neoprenes.

### Neoprene AG

Neoprene AG is a gel polymer designed to provide improved application properties. The unique characteristic of Neoprene AG is that dispersions in solvent exhibit thixotropy, permitting the formulation of high solids, high viscosity mastics that are easily applied by troweling or extruding, but resist slump or flow after application. The adhesives are buttery, not stringy. Low viscosity (lower solids) formulations based on Neoprene AG have better spray characteristics (no cobwebbing) than other neoprenes. Neoprene AG and AD. However, formulations compounded for easy application generally have lower cohesive strength and adhesion.

Neoprene AG is especially useful in high solids, high viscosity adhesives. It can be used alone or in conjunction with other neoprenes. Of particular utility is Neoprene AG/W blends, in which Neoprene W serves to decrease cost and increase tack at the expense of application properties.

The spray properties of low viscosity Neoprene AG formulations are considerably better than those of the other neoprenes. This is particularly so at low atomization pressures ( 70 psi). As with other neoprenes, the critical factor in the solvent blend selected. Preferred solvent systems for Neoprene AG are combinations of oxygenated solvents with a 3.5 to 5.5 hydrogen bonding index and 7.5 to 9.8 solubility.



Neoprene AH

Neoprene AH is an acrylic copolymer of chloroprene which and be peptized in aliphatic solvents to form stable colloidal dispersions. This enables one to formulate high solids systems exhibiting the application advantages of latex systems with the bond strength development of solvent adhesives. Neoprene AH dispersion adhesive formulations can be designed to develop hot bond strength equivalent to types AC and AD, but at the expense of tack time. The use of aliphatic solvents alone, without toluene or ketones, offers the advantages of low cost, acceptability of stability and the capability to bond substrates such as polystyrene which are sensitive to aromatic or ketone solvents.

Table 5.3 International suppliers of Neoprenes

Neoprene Type	W	AC	AD	AF	AG	AH
<b>Manufacturers:</b>						
Dupont	✓	✓	✓	✓	✓	✓
Petrolex	✓					
Distugil: Butaclor (France)	✓	✓	✓			
Bayer: Bayprene (Germany)	✓	✓	✓			
Denki Kagaku: Denkaprene (Japan)	✓		✓			

Table 5.4 Suppliers of Neoprenes in Thailand

Neoprene Type	W	AC	AD	AF	AG	AH
Suppliers						
Dupont Far East Inc., Thailand Branch	✓	✓	✓	X	X	X
Bayer Thai Co.,	X	✓	✓	X	X	X

✓ = EX-Stock

X = NO-Stock



### 5.3 Resins

Resins are the principal ingredients after the neoprene itself. They provide specific adhesion, allow neoprene to bond to itself under low pressure when tack free to the touch ("contact adhesive"), and improve cohesive strength. The main resins used are the t-butyl phenolics. They provide much higher heat-resistance than other classes of resins with similar melting points. Other resins used include terphenolics, polyterpenes, rosin esters, and coumarone-indene resins.

Heat-reactive alkyl phenolic resins, particularly the t-butyl phenolic variety, are generally used at 35-50 phr level to achieve a good compromise between tack and heat-resistance. Resin levels above 50 phr historically have been avoided.

The high heat-resistance achieved by this class of resin is due to their reactivity with the magnesium oxide normally present in neoprene adhesives. The magnesium oxide resinate or resin salt is infusible, but decomposes above 200°C. The resinate reduces the thermoplasticity of the adhesive system and makes possible adhesives with useful bond strengths up to about 180°F. The resinate also promotes solvent release, aiding early bond strength development. The optimum level of MgO required for this reaction is 10 phr on resin, corresponding to 4 phr on the rubber at a resin level of 40 hr.

Table 5.5 International suppliers of t-Butyl Phenolic Resins.

Supplier	Product
Ashland Chemical Co., Columbus, Ohio.	6690 640 6403
Reichhold Chemicals Inc., White Plains, N.Y.	Super-Beckacite 1001 Super-Beckacite 1054 Varcum 921 Varcum 871
Schenectady Chemicals, Inc., Schenectady, N.Y.	SP - 103 SP - 134 SP - 144 SP - 154
Union Carbide Plastics Co., New York, N.Y.	CKM-1634 CKM-1734

Table 5.6 Suppliers of Phenolic Resins in Thailand

Supplier	Product
1. Schenectady Chemicals, Inc, New York Represented by Du Pon Far East Inc., Thailand	SP 134 SP 154
2. Union Carbide Plastic Co., New York Represented by Union Carbide Thailand	CKM - 1634 CKM - 1734

Note: 1. CKM - 1634 is recommended where a good balance of high peel strength and good hot strength is required.

2. CKM - 1734 is recommended for adhesion application demanding excellent hot strength property and being essentially from unreacted butyl phenol.

3. SP - 154 is required for a very high heat resistance strength

4. SP - 134 is like SP 154 except less cohesive strength

#### 5.4 Metal Oxides

Metal oxides serve a number of roles in adhesive compounding (Table 5.7)

1. They are reactants for t-butyl phenolic resin. Fine particle size, high activity magnesium oxide is preferred.

Oxides of calcium, lead, lithium, etc. have also been used. Both calcium oxide and litharge react with t-butyl phenolics to form resinous products which do not melt, yet which are soluble in neoprene and give higher heatresistance. They have several disadvantages, however. Both give cements with relatively poor stability. The films with calcium oxide have better tack retention and do not heat-activate readily. They can be reactivated easily by solvent. Litharge films cannot be heatactivated satisfactorily, and cannot be used in many applications because of toxicity.

2. They are acid acceptors. The small amounts of HCl given off during curing and aging of neoprene must be accepted by the adhesive film. This is particularly important in those applications where the film is deposited on acid sensitive materials, such as fabrics like rayon and cotton. Both magnesium and zinc oxide fill this function with the combination being synergistic.

3. They are processing stabilizers. They are mixed to retard scorch in processing.

Table 5.7 Role of Metal Oxide

Resin reactant	MgO, PbO, CaO, etc.
Acid acceptor	MgO, ZnO
Scorch retarder	MgO
Curing agent	ZnO, MgO

Note: Suppliers of metal oxides are widely available  
in Thailand



## 5.5 Solvents

Solvents are among the most important compounding ingredients used in the formulating of contact adhesives. They affect the rate of strength development, open time, cost, adhesion, application properties, solution viscosity, and to some degree, ultimate strength. The typical solvent systems used in neoprene adhesives are blends of aliphatic and aromatic solvents with varying portions of such oxygenated solvents as ketones and esters. The most popular solvents are hexane, toluene, methyl ethyl ketone (MEK), and acetone. Chlorinated solvents such as methylene chloride are used when nonflammable systems are needed.

Dupont developed solvent system for neoprene that is a normally basic principle for selection of the solvent as follows:

### Solvent System For Neoprene

A simple graphical method for predicting the solubility of neoprene in a given solvent or blend of solvents is described here.

We describe a technique which takes much of the guesswork and trial and error experimentation out of

- (a) predicting the solvent strength of a proposed blend
- (b) modifying the characteristics of a blend in some desired direction
- (c) designing entirely new blends.

## Predicting The Solvent Strength Of Blends

Table C.1      some useful characteristics of 22 of the solvents commonly used in the preparation of neoprene adhesives, cements and coatings. The first seven are "true" solvents; that is, they dissolve neoprene completely by themselves. The first column of numbers represents "solvent strength" (SS), or the relative power of a fluid to dissolve raw neoprene (the scale is explained at the foot of the table). True solvents, such as toluene and xylene, have a rating of 10; some esters and ketones have ratings of 9 or 8; this means they give a cloudy solution or one that tends to separate into two phases with some neoprenes and give clear solutions with others, depending on the molecular weight, gel content and other characteristics of the polymer. Many solvents and blends used in commercial neoprene solutions have a rating of 9 on the SS scale.

Solvents with ratings below 8 are useless as neoprene solvents by themselves; however, they have a definite place in this study because many such "weak" solvents serve as tolerable diluents in blends with true solvents. In fact, the chemist can combine two or more of the weak solvents, properly selected, to make useful solvent blends for neoprene.

## The Basic Tools

The graphical prediction technique is new in this field but the tools on which it is based (solubility parameter and hydrogen bonding strength) are familiar to the solution chemist. Numerical solubility parameters ( $\delta$ ) have been published for many common solvents. Hydrogen bonding strength, on the other hand, is usually reported as low, medium, or high (see Table C.1). We have derived more precise values for the solvents in Table I. On a scale running from 1.0 to 10.0, "low" hydrogen bonding strength is represented by numbers from 1.0 to 4.0, "medium" from 4.0 to 7.0, and "high" from 7.0 to 10.0. The adjusted values assigned to each solvent (or blend) are referred to as "hydrogen bonding index" ( $\gamma$ ); they do not necessarily fit other scales of hydrogen bonding parameter or strength published elsewhere. The column headed " $\gamma$ " in Table 3 gives the new indices.

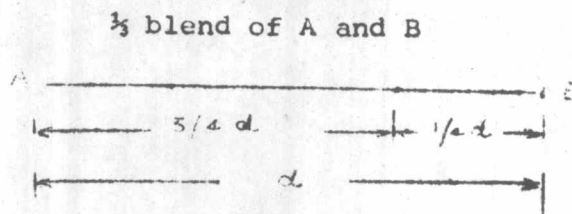
Fig C.1 is the key to graphical solvent strength predictions for Neoprene AC, Neoprene AD and the W neoprenes. The chart was developed experimentally on the basis of the observed solvent strengths of the individual solvents as well as those of numerous blends.

## Two-Component Blend

The apparent coordinates (geometric center of the "clear solution" area) for raw W types of neoprene are  $\delta = 9.5$  and  $\gamma = 3.5$ . All the true solvents are grouped in an area surrounding

this point and representing a solvent strength of 10. Any blend of solvents for neoprene must have weighted average  $\delta$  and  $\gamma$  values which place it in or near this area in Fig C.1. Note that the contour shown is based on Neoprenes AD-30, WHV-A, WD and AC Hard. With lower molecular-weight polymers, such as the softer grades of AC and AD and Neoprene W, WM-1, or WRT, any given solvent will have a slightly better solvent strength rating than Table C.1 indicates.

The point described by the average  $\delta$  and  $\gamma$  for a blend of two solvents always lies on a line connecting the two single solvent points. The blend point is closest to the point representing the larger of the two constituents. For example, for a blend of one volume of A and three of B, the new blend point is located as follows:



It can be seen at a glance (on Fig C.2) that a 1/1 blend of toluene and aniline lies in the "clear solution" area. Even a 3/1 blend of aniline and toluene ( $\frac{3}{4}$  of the distance from toluene to aniline) is still in the solution area. The chemist can design literally hundreds of two-component blends having a "10" rating by simply looking at Fig C.2. Considering 100 volumes of benzene

as the true solvent starting point, we can predict that it will still dissolve the aforementioned types of neoprene even if we add 600 of aniline, or 40 of Methyl Cellosolve, or 100 of acetone, or 180 of MEK, or 1000 of DIBK, etc.

### Three-Component Blend

The coordinates for a three-component solvent blend can be located graphically or calculated mathematically. In the latter case  $\delta$  and  $\gamma$  are calculated independently and are then plotted. In the graphical method, both are averaged simultaneously. As a sample problem, let locate the coordinates for

#### Blend A:

Nitropropane .....	10 Parts by volume
MEK .....	20 parts by volume
Turpentine .....	30 parts by volume
	60

#### Mathematical Method:

Look up  $\delta$  and  $\gamma$  for each of the solvents (in Table C.1) Then calculate the volume fraction ( $v$ ) of each solvent in the blend:

Solvent	$\delta$	$\gamma$	$v$
Nitropropane	10.7	1.9	1/6
MEK	9.3	5.4	2/6 or 1/3
Turpentine	8.1	3.8	3/6 or 1/2

Now substitute these volumes in the equations

$$\delta = \delta_1 v_1 + \delta_2 v_2 + \delta_3 v_3$$

and

$$\zeta = \zeta_1 v_1 + \zeta_2 v_2 + \zeta_3 v_3$$

then

$$\begin{aligned} \delta_A &= 10.7(1/6) + 9.3(1/3) + 8.1(1/2) \\ &= 1.78 + 3.10 + 4.05 \\ &= 8.93 \end{aligned}$$

and

$$\begin{aligned} \zeta_A &= 1.9(1/6) + 5.4(1/3) + 3.8(1/2) \\ &= 0.31 + 1.80 + 1.90 \\ &= 4.01 \end{aligned}$$

Plotting  $\delta_A$  and  $\zeta_A$  on Figure 2 (point A) we find that the blend lies in the clear solution area.

Graphical Method (same blend "A")

In the graphical method, the  $\delta$  and  $\zeta$  values for the solvents are not needed. Trace the dots for the three solvents on a piece of tissue paper. Start with any one of them and "build" the blend with a pencil and ruler. For example, start with nitropropane (see Figure C.2) and "add" MEK to make a 1 nitropropane/2 MEK blend. Since MEK is the larger, move 2/3 of the distance from nitropropane to MEK; point "B" and turpentine. Note that A and C are the same, proving the accuracy of the graphical method.

## Four-Component Blend

Blend D:

Nitropropane . . . . .	10
MEK . . . . .	20
Turpentine . . . . .	30
Acetone . . . . .	<u>25</u>
	85

Point Crepresents the first three components as if they were one solvent. We may therefore treat the new blend D as a combination of 60 parts of C with 25 parts of acetone. Therefore we move 60/85 (or 70%) of the distance from acetone to C (because C is the larger), and we have point D ( $\delta_D = 9.25$  and  $\gamma_D = 4.6$ ). Obviously the acetone has moved the blend into the "borderline" area; but it is equally evident that 15 parts of acetone with 60 of blend C would be tolerable.

In the mathematical method, the introduction of acetone changes all the volume fractions:

$$\begin{aligned}\delta_D &= 10.7(10/85) + 9.3(20/85) + 8.1(30/85) + 10(25/85) \\ &= 9.25\end{aligned}$$

$$\begin{aligned}\gamma_D &= 1.9(10/85) + 5.4(20/85) + 3.8(30/85) + 5.9(25/85) \\ &= 4.57\end{aligned}$$

Here again the accuracy of the graphical method is adequate.

### Graphical v.s. Mathematical Method

The graphical diagraming of a solvent blend can be done in any order, provided the chemist remembers that

- (a) total volume increases as each component is "added"
- (b) a new blend point must be closer to the larger of the two portions being "combined" graphically.

The accuracy of the graphical method is limited only by the size of the chart and the accuracy with which distances are calculated and measured. The need for using ruler and sliderule (instead of merely estimating distances by eye) increases with the number of components in the blend. Otherwise the graphical method is definitely preferable because specific values for  $\alpha$  and  $\beta$  need not be considered at all. The composition of the blend is converted directly into a solvent strength rating by means of Fig C.2. Of course neither method applies unless the solvents in a proposed blend are non-interacting and completely miscible; if two solvents have  $\alpha$  values differing by more than 4.0, they may be immiscible.