



## reinforcing phenolic resins

*Due to the ease and diversity of reactions, there are many products manufactured from phenols. One very useful group of materials formed from the reaction of phenol and formaldehyde is known as phenolic resins. Akrochem offers a broad line of phenolic resins that find use in rubber as outstanding tackifiers (non-heat reactive), heat reactive resins through methylol (-CH<sub>2</sub>OH) groups (used in polychloroprene adhesives and as crosslinking resins), and heat reactive through methylene (-CH<sub>2</sub>-) crosslinking in what are called reinforcing phenolic resins. This edition of "Solutions" will concentrate on the reinforcing resins - those resins that contribute hardness, stiffness, and tear resistance to rubber compounds while reducing compound processing viscosity.*

A two-step process forms reinforcing phenolic resins and thus they are often referred to as "two-step resins." The first step combines a phenol with formaldehyde to form a novolak resin (see Step 1). Novolaks are thermoplastic resins with methylene bridges between the phenolic groups. They melt under heat but do not react further unless a methylene (-CH<sub>2</sub>-) donor is available.

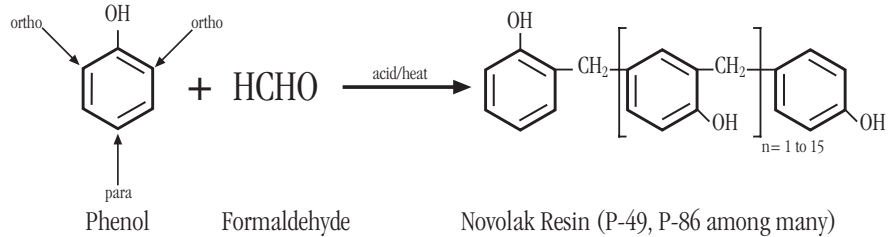
Novolaks usually have an average molecular weight between 400 and 1500. If there are alkyl groups (4 to 8 carbon units typically) substituted in the ortho and/or para position of the phenol, the novolak resists further reaction and would not be a thermosetting reinforcing resin. These alkyl novolaks are represented by the many tackifying phenolic resins. It should be noted that the resin (Akrochem P-49 and P-86) portion of reinforcing phenolic resins is only a moderate tackifier. If good tack is needed in a compound, it is best to get a true tackifying phenolic resin (ask Akrochem Technical Service for help in choosing a proper tackifying resin).

When there are additional bonding sites available (both ortho sites and the para site), the simple phenolic novolak resins (again, two examples are Akrochem P-49 and P-86 resins) can be further reacted to form a complex, three-dimensional, thermoset resin (Step 2). In this reaction, the novolak resin is crosslinked with a methylene (-CH<sub>2</sub>-) donor (either hexamethylenetetramine [HMT] or hexamethoxymethylmelamine [HMMM]) to form a cured resin.

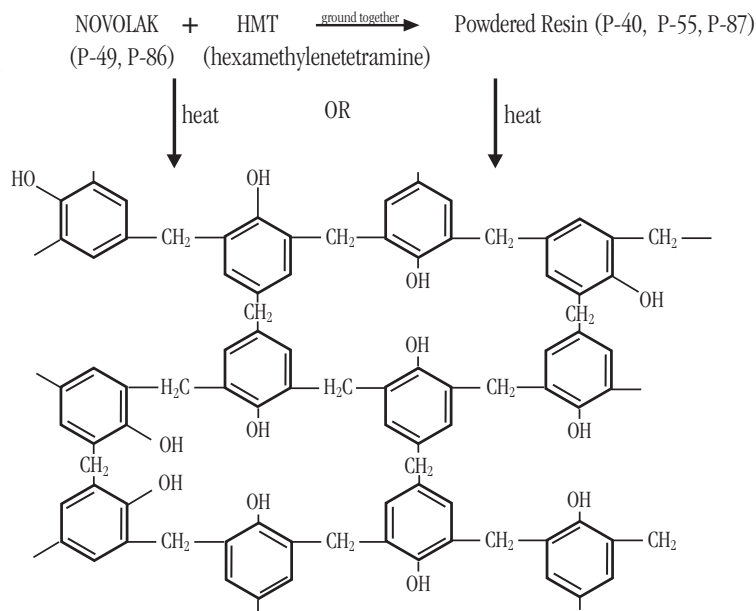
The cured resin is heavily crosslinked (depending on the amount of methylene donor) so a large increase in hardness results. Other cured rubber properties affected by the resin include much-improved chemical resistance, higher stiffness values, better tear (especially trouser tear), and better Demattia flex-cracking resistance (compared to alternate ways of hardening a compound). Compression set is usually negatively affected but not as much as plastic hardeners like PVC or styrene.

While these reinforcing resins have been available to the rubber compounder for many years there are still a lot of questions regarding the best way to use them. In this Solutions, we'll discuss the types of reinforcing resins available, how best to use different resins in various applications, mixing methods for these reactive phenolics, and miscellaneous information useful to a rubber compounder.

## step 1 – making a phenolic resin or “novolak”



## step 2 – making a cured resin



### AKROCHEM REINFORCING PHENOLIC RESINS

Akrochem Resin	Curable?	% HMT	Modifier Oil	Scorch Inclined Plate Flow @ 125°C, mm	Cure Rate Hot Plate Cure @ 160°C, sec	MP, °C
P-40	yes	6.0 – 8.0	none	20 – 40	20 – 40	82.2
P-49	no	----	tall oil	----	----	95.0
P-55	yes	6.5 – 8.5	tall oil	40 – 70	30 – 50	67.8
P-86	no	----	cashew nut shell	----	----	95.0
P-87	yes	6.0 – 8.0	cashew nut shell	40 – 60	25 – 40	66.7

**Form:** The non-reactive (non-curable) resins, P-49 and P-86 are hard, flake resins. The melt point is high enough that care must be taken to make sure they get thoroughly melted during mixing.

The curable resins are powders since the HMT or “hexa” is ground into the pulverized resin. The combining with hexa lowers the melt point (compare P-86 to P-87). The modifying oil also lowers the melt point (compare the unmodified P-40 to the tall oil-modified P-55). Thus, the curable powdered resins can be added to a second pass through an internal mixer or on a mill.

All phenolic resins should be stored in cooler areas away from heat sources. It is the nature of resins to want to coalesce into a solid mass. Hot storage areas will accelerate the problem as will the weight from stacking bags of resin on top of each other. For this reason, drum packaging for volume usage is sometimes a better choice than bags.

**Mixing:** The reinforcing resins have always been used to harden or increase durometer while improving the processing of a compound. Compared to a heavily black-loaded compound, resin-and-black-loaded 90 duro compounds mix much easier with the handling characteristics of a 60 duro stock. Several issues concerning mixing should be discussed and kept in mind when designing a resin-reinforced compound.

P-40, P-55, and P-87 are thermosetting resins. The crosslinking begins to occur rapidly around 250°F. Care must be taken not to mix these reactive resins for any length of time above 240°F-250°F. Processing (scorch) time will suffer if the mix gets too hot. Typically, a resin-filled batch will begin to soften dramatically once the resin hits melt point and thus the mix-temperature-climb will slow down. High duro, black-and-resin-filled batches can often be single-pass mixed and still dumped under 250°F. If a higher mixing temperature is needed to incorporate a “hard” black like N-220, it would be wiser to use the non-reactive resins like P-86 and P-49 in the masterbatch portion of a two-stage mix. These resins will provide easier processing when melted but can be mixed to any temperature without concern. The crosslinking agent (usually HMT) is then added during the second stage along with the other curatives.

Some other thoughts on reinforcing resin mixing:

- 1) If one wants to add a small amount of reactive resin (5-10 phr) to a mix, but still wants to avoid the heat of the masterbatch, add the resin in the second stage. However, the resins should have a filler to dry them up once they melt. If added in the second pass where minimal materials are being added, the resins may stick to the rotors of an internal mixer or the back roll of a mill unless some filler is added to absorb the resin (the affinity of these resins for metal will be discussed later). It is best to pick a non-reinforcing filler (preferably moved from the first pass) to add along with the resin to prevent the rotors or mill rolls from getting “gunked up.”
- 2) By the same reasoning, if a large amount of resin is being added at any point in the mix, make sure there is loose filler available at the time of melt. Adding half the filler and resin at two points in the mix is often the best solution.
- 3) The reinforcing resins will soften a batch when it is at processing temperatures. This allows oil-free, high durometer batches to be easily processed. But being thermoplastic resins prior to cure, the resin as well as the mixed batch will become quite hard at room temperature. At high resin loadings, the batch will be extremely stiff when cold. With this in mind, cold stock should not be added too rapidly to a mill or mixer. Ease it in initially until enough of the stock has softened to allow the rest of the hard stock to be added. This will also help prevent excess heat history in the stock. It is better to use warm mills for high-resin batch processing rather than ice cold. A cold mill will only stiffen the batch and make it harder to work with.
- 4) Calendar rolls should be run a little warmer than normal to keep the resin softened and improve sheet smoothness.

### Modifications:

Most of the reinforcing phenolic resins used by the rubber industry are the modified type. There are several reasons or advantages to using the modified resins rather than a straight phenolic:

- a) The long hydrocarbon chain present in the modifiers provides better solubility in rubber. Unmodified phenolic resin is extremely polar and limits its rubber compatibility to primarily high ACN nitriles.
- b) The modifier acts to make the cured phenolic resin more pliable. This gives the final product more flexibility, especially at higher temperatures, than an unmodified resin (similar to a rubber providing better impact resistance to a plastic). Dynamic properties are enhanced.
- c) Chemical resistance to acids and bases is improved due to the water resistance of the “fatty” hydrocarbon chain.

The two major modifications to Akrochem reinforcing resins are cashew nutshell oil - CNO (CNO is in P-86 and P-87) and tall oil - TO (TO is in P-49 and P-55). The differences that result from use of either modifier type will be discussed in more detail but here are a few of the major differences:

- a) CNO is a phenolic resin itself and can enter into the crosslinking reaction. It also has a double bond site in the side chain that may also be crosslinked. Tall oil does not help the phenolic crosslinking; it actually ties up some of the reactive phenol sites. For this reason, the CNO modified resins cure faster and to a higher duro than the TO products.
- b) Rubber compatibility is affected. Unmodified P-40 resin is compatible only with high ACN nitriles. CNO-modified P-87 resin is very compatible with all nitriles and to a certain extent with less polar elastomers like SBR and CR. TO-modified P-55 is more compatible with SBR and EPDM. As will be seen later, compatibility of any of the modified phenolics in less-polar elastomers can be increased by blending approximately 20 phr of a nitrile into the SBR or CR where the NBR functions as a compatibilizer.
- c) Unmodified P-40 and (TO) P-55 resins give the best color and will cure to a light-to-medium tan color. P-87 (CNO) resin cures to a dark tan-to-brown color. Use P-55 for most color applications.

### Some Examples of Reinforcing Resins in Rubber:

Several formulas were used to add reinforcing resins. A nitrile (NBR), a polychloroprene (CR), an EPDM, and an SBR were pre-mixed and the resins added on a mill hot enough to melt the non-reactive resins like P-49 and P-86. The NBR rubber was also blended with CR and SBR such that NBR made up 20 phr of the rubber hydrocarbon. This will show the effect of using NBR to compatibilize the resin with other polymers. Formulas are available upon request but are not really critical to the use of reinforcing resins.

These resins are convenient in that a favorite in-house compound can be hardened quickly by the addition of resin on a mill. Compounding expertise is not needed with these. (There are a few interacting chemicals for which you want to watch. These will be mentioned later in this brochure.)

		Shore A Durometer			
P-87 PHR	Added	<u>0</u>	<u>10</u>	<u>20</u>	<u>30</u>
NBR		55	60	70	82
NBR + 10 phr MgO		---	---	73	---
CR		58	71	80	89
CR/NBR (80/20)		58	---	---	95
EPDM		55	64	68	73
SBR		60	74	81	86
SBR/NBR (80/20)		59	---	---	88

		Shore A Durometer			
P-55 PHR	Added	<u>0</u>	<u>10</u>	<u>20</u>	<u>30</u>
NBR		55	61	65	74
NBR + 10 phr MgO		---	---	70	---
CR		58	75	82	84
CR/NBR (80/20)		58	---	---	95
EPDM		55	62	65	66
SBR		60	68	71	76
SBR/NBR (80/20)		59	---	---	85

- P-87 normally provides a higher durometer than P-55. This is to be expected since the cashew oil modifier does not alter the reactivity of the phenol (and may actually enter into the crosslinking) while the tall oil modifier does take up a phenol reactive site.
- Rule-of-thumb would use about 1.2 phr of P-87 per point Shore A durometer increase in all but EPDM polymers. P-55 would use about 1.5 phr. Compatibility issues and total loadings can cause this rule to vary some.
- For extra hardness without using more resin, try adding magnesium oxide (MgO). It has no effect on the scorch but boosts the duro (probably by crosslinking the -OH groups of the phenols). The effect is less noticeable in the above lower duro compounds, but in a hard, 40 phr P-87 loaded nitrile, the duro went from 54 Shore D to 61 Shore D by adding 10 phr MgO. CaO works similarly.
- Adding NBR to SBR or CR increases compatibility and improves duro. The SBR and CR rheometer curves without NBR show a waviness that is an indication of two different cure phases. Once NBR is added, both SBR and CR have smoother, one-phase cures. In all four examples where NBR was used to compatibilize the phenolic resin and the polymer, the resulting durometer is higher than either individual compound, showing a definite synergy.

340F Cure Data T<sub>2</sub> (sec) / Maximum Torque

P-87 PHR Added	<u>0</u>		<u>10</u>		<u>20</u>		<u>30</u>	
	<u>T<sub>2</sub></u>	<u>Max</u>	<u>T<sub>2</sub></u>	<u>Max</u>	<u>T<sub>2</sub></u>	<u>Max</u>	<u>T<sub>2</sub></u>	<u>Max</u>
NBR	85	52	59	51	57	53	53	48
NBR + 10 phr MgO	---	---	---	---	55	52	---	---
CR	78	70	49	74	42	85	37	100
CR/NBR (80/20)	77	65	---	---	---	---	41	77
EPDM	120	49	52	43	37	32	35	23
SBR	130	48	53	50	39	56	32	60
SBR/NBR (80/20)	135	49	---	---	---	---	38	57

340F Cure Data T<sub>2</sub> (sec) / Maximum Torque

P-55 PHR Added	<u>0</u>		<u>10</u>		<u>20</u>		<u>30</u>	
	<u>T<sub>2</sub></u>	<u>Max</u>	<u>T<sub>2</sub></u>	<u>Max</u>	<u>T<sub>2</sub></u>	<u>Max</u>	<u>T<sub>2</sub></u>	<u>Max</u>
NBR	85	52	77	48	71	50	67	48
NBR + 10 phr MgO	---	---	---	---	73	54	---	---
CR	78	70	56	77	57	77	56	76
CR/NBR (80/20)	77	65	---	---	---	---	54	70
EPDM	120	49	72	44	66	37	56	31
SBR	130	48	84	49	50	53	57	51
SBR/NBR (80/20)	135	49	---	---	---	---	57	59

- P-55 will provide more scorch time (T<sub>2</sub>) than P-87 (compare T<sub>2</sub> for NBR – 30phr for P-87 and P-55). Hardness is not as good but adding MgO or additional resin can make that up.
- As reinforcing resins are added, the state-of-cure (max torque) remains the same or increases. This indicates one of the advantages of the crosslinked resins over plastics. At higher temperatures, most plastic-containing formulas have a lower state-of-cure and a lower durometer. Resin cures soften a little but to a lesser extent. Note that in EPDM the state-of-cure does drop due to severe incompatibility.
- Another way to improve scorch is to use P-86 or P-49 resins with HMMM instead of HMT. HMMM (Cyrez® 966 is an example) will crosslink the phenolic resin with no loss in scorch compared to straight unreacted resin. Cure time is slower (and thus the duro is lower at an equivalent cure time) than HMT. To bring the HMMM cured results close to HMT properties use longer cure times, higher % loadings of HMMM (use 10% on resin instead of the HMT norm, 8%) or simply add more P-49 or P-86 along with 10% HMMM resin (rule-of-thumb: use 20% more P-49 or P-86 with HMMM than is used with HMT).

<u>40 phr total resin and cure in NBR</u>	<u>T<sub>2</sub></u> <u>@ 350°F</u>	<u>T<sub>90</sub></u> <u>@ 350°F</u>	<u>Duro @ 6' cure</u> <u>Shore D</u>
P-86 plus 8% Hexa (HMT)	0.75	2.93	54*
P-86 plus 8% HMMM	1.31	6.12	51*
P-86 only	1.28	2.62	19 (65 Shore A)

\*When fully cured, 15' @ 350°F, both are 55 D

- The T<sub>2</sub> time, or scorch, drops quickly upon addition of the curable resin. Regardless of the original scorch, all the polymers settle into approximately the same scorch range. This is because the reinforcing phenolics cure at their own rate, independent of the polymer cure. You can't slow the sulfur cure in order to slow the phenolic cure. Also note how NBR is the least affected scorchwise by the resin. While NBR without resin has only the third best scorch (best being slower scorch) among the 4 polymers, it has the best scorch after resin is added, probably a function of compatibility.
- Acid materials will speed up the reaction between phenolic resins and HMT. Salicylic acid (Akrochem Retarder SAX) will increase cure rate significantly. You might have a cement with high resin loading you want to accelerate. By the same token, if you are having scorch problems with a phenolic resin, make sure there are no acid retarders (salicylic, benzoic, or phthalic anhydride) in the formula – they will not retard; they will possibly scorch. Also watch for air-floated clays (“hard” and “soft” clays). These have a pH around 4.7 and can acidify a stock and cause scorch (for this reason, don't use air-floated clays in peroxide cures either. Cure is often flat-lined by acidic clay).
- Other retarders like CTP (cyclohexyl thiophthalimide) have no effect on the cure rate of a phenolic resin. Only the sulfur portion of the cure is slowed.

### Improvement in Adhesion Properties Using Reinforcing Resins:

Reinforcing resins can form adhesive hydrogen bonds with metals, fabrics, plastics, wood, and rubber. For many years a wide variety of adhesives have been made by simply blending nitriles and curable phenolic resins. These can vary from rigid structural adhesives to flexible, knife-coated fabric coatings.

An example of a simple cement formula might look like:

	%
Nitrile polymer	15
P-87 Resin	15
MEK solvent	70

This simple formula will bond many unlike surfaces such as wood-to-rubber, fabric-to-rubber, rubber-to-rubber, and rubber-to-metal. Variations for bonding systems include:

- Compound the nitrile portion with fillers and a cure system for better bonds and greater heat resistance. Solvate any nitrile compound (one with silica filler and minimum plasticizers works best) in MEK (adding a little methyl alcohol will help absorb water) then stir in P-87 resin.
- Add a phenolic tackifying resin in addition to the reinforcing resin to create a “tack” cement that holds objects together until cure takes place.
- Make a patching compound by adding P-87 or P-55 to the rubber you want to patch, and then add a room temperature accelerator like Akrochem ZDBCX to make an easy-to-cure patch. Again, tackifying phenolic resins like P-90 or P-133 will help hold the patch in place.
- Add P-55 or P-87 to rubber to boost metal or fabric adhesion. These resins act similar to resorcinol and hexa to improve fabric bonding. They also have a strong attraction to metal. The presence of the resin allows a more intimate, wetted contact surface between the rubber and the surface to be bonded. A higher surface energy created by the presence of the phenolic resin helps attract metals or RFL fabric systems to form hydrogen bonds. Simply adding

3-5 phr of a reinforcing resin to a formula will often improve the bond strength by 20% or more and in some cases, be the difference between a good bond and an inadequate bond.

### Other Tips for Using Reinforcing Resins:

- Phenolic resins will interfere with peroxide cures. This is not to say that the reinforcing resins can't be used with peroxides. They can provide some advantages like improved tear strength, which is often a problem in peroxide cures. To use the phenolics with peroxide, don't use over 15 phr of resin and if the same state-of-cure is needed after the phenolic resin is added, add more peroxide to compensate for the cure interference.
- Adding additional HMT beyond the normal 6.5 – 8.0% will have little effect on durometer but will improve abrasion and chemical resistance.
- FDA Status: The FDA regulations regarding rubber in repeated contact with food are covered under CFR 21, Section 177.2600. Under plasticizers, phenol-formaldehyde resins are listed. Akrochem resins P-40 and P-55 (as well as P-55's non-curing form, P-49) are acceptable for use in FDA formulations. The cashew nut oil-modified P-86 and P-87, strangely enough, are not FDA. Since phenolic resins are listed as plasticizers in an FDA formula, they can be 30% of the total formula weight as permissible for plasticizers under the FDA regulations. The curing phenolic resins have the distinct advantage over other plasticizers in that many FDA parts must have extraction tests performed on them. The reinforcing phenolics will provide a plasticizing action during processing and then become essentially non-extractible once cured.
- One interesting use of reinforcing phenolic resins is as a binder of particulate ground rubber scrap (primarily tire regrind). The powdered resin serves as the bridging and bonding medium between regrind particles providing improved physical properties in the finished part. A similar application uses reinforcing phenolics to compatibilize woodflour and polyethylene plastic. Brake pads and grinding wheels are usually bound together and hardened by phenolic resins.

**Conclusion:** Reinforcing phenolic resins are a handy tool for the rubber chemist. They can harden a batch quickly and with relative ease. They can allow easy processing of 90 duro compounds. They can bind and reinforce various systems. And finally, they can improve adhesion properties of many products. This versatility extends to all the phenolic resins that we will be examining further in future Solutions.



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