



Compounding, Mixing and Processing Peroxide-Cured Viton[®] Made with Advanced Polymer Architecture

General Comments

The new Viton[®] fluoroelastomer polymers made with **Advanced Polymer Architecture** (APA) technology have been designed to provide an excellent balance of processing and physical properties. Compared with earlier peroxide cured types of Viton[®], the APA polymers show faster and more efficient curing with good mold flow, outstanding mold release and low mold fouling. These improvements are due to the modified molecular weight distributions, improved cure site monomers and unique end group chemistry of the new polymers.

The molecular architecture changes require some modifications to be made in compounding and mixing these polymers to maximize the benefits available from the APA types. This document outlines some guidelines and techniques that should be employed to obtain the maximum advantages from the new Viton[®] polymers made with APA.

The new, peroxide cured APA polymers (and product families) are:

65 ML @ 121°C polymers

- Viton[®] **GF-600S** (formerly VTR-8600)
- Viton[®] **GBL-600S** (formerly VTR-8650)
- **VTR-8500** (to become GLT-600S)
- **VTR-8525** (to become GBLT-600S)
- **VTR-8550** (to become GFLT-600S)

25 ML @ 121°C polymers

- **VTR-8605** (to become GF-200S)
- Viton[®] **GBL-200S** (formerly VTR-8655)
- **VTR-8505** (to become GLT-200S)
- **VTR-8555** (to become GFLT-200S)

Compounding the New Peroxide Curable Polymers

Peroxide Selection and Level

As with older versions of peroxide curable Viton[®], the preferred peroxide for curing the APA polymers is Varox[®] DBPH50 (or Lupercos[®] 101XL45) which gives an excellent balance of fast cure rate and low compression set.

- Alternatively, Varox[®] 130XL (or Lupercos[®] 130 XL, Trigonox[®] 145 45B) can be used when a slower, safer cure is needed.

- Varox[®] DBPH50-HP is an alternative peroxide which has shown good utility in peroxide cured APA polymers. DBPH50-HP peroxide is slower curing with a longer ts2 time than Varox[®] 130XL, and has extended scorch safety.

Provided the level of peroxide is above a minimum critical level, peroxide acts as an accelerator increasing the rate of cure with little effect on the state of cure. Because of the more efficient curing chemistry of the APA polymers, less peroxide is necessary to effectively cure the polymer. For processes where scorch safety is critical, such as transfer and injection molding, the recommended starting point level of peroxide (DBPH50 or Varox[®] 130XL) is between 1.25 and 1.5 phr. Slightly elevated levels of peroxide can be used in processes such as compression molding to increase cure rate when scorch is less of an issue. Higher levels of peroxide, above 3 phr, decrease scorch safety without changing the compound physical properties.

A study comparing Varox[®] DBPH50, Varox[®] DBPH50-HP, Varox[®] 130XL, Varox[®] 802-40KE and Varox[®] DCP-40KE was done and can be viewed on Table 3 of the Viton[®] GF-600S product data sheet.

Note: Varox[®] DBPH50 is a 45% active dispersion of 2,5-dimethyl-2-5-di-(t-butyl-peroxy)hexane
 Varox[®] DBPH50-HP is a 45% active dispersion of 2,5-dimethyl-2-5-Di-(t-butyl-peroxy)hexane
 Varox[®] 130XL is a 45% active dispersion of 2,5-dimethyl-2-5-Di-(t-butyl-peroxy)hexyne-3
 Varox[®] 802-40KE is a 40% active dispersion of alpha-alpha'-Di(t-butylperoxy)-diisopropylbenzene
 Varox[®] DCP-40KE is a 40% active dispersion of Dicumyl peroxide

Co-agent Selection and Level

The preferred co-agent for the APA polymers is DIAK[™] No.7 (triallyl isocyanurate -TAIC,). APA polymers need to be compounded using triallylisocyanurate (TAIC, DIAK[™] No.7) to achieve optimal properties, compression set resistance and processing. Compounds using other coagents like trimethallylisocyanurate (TMAIC, DIAK[™] No.8) or triallylcyanurate (TAC) do not cure as efficiently and yield vulcanizate having inferior properties and processing with a higher incidence of mold sticking and fouling. Therefore DIAK[™] No. 8 (trimethallyl isocyanurate - TMAIC,) should **NOT** be used. APA polymers cured with DIAK[™] No. 8 exhibit poor states of cure, poor resistance to compression set and have increased mold sticking & fouling.

The level of DIAK[™] 7 affects the state of cure with little effect on the rate of cure.

- The standard level of DIAK[™] No. 7 is 3 phr. A lower level of TAIC will result in lower modulus and hardness and higher elongation with a minimal impact on compression set, and general lower levels of TAIC showed improved processing vs. high levels
- Higher levels of DIAK[™] No. 7, up to 5 parts, will increase modulus and hardness, modestly improve compression set, and increase the flow (plasticizer effect) of the APA polymers, however it should be remembered that high levels of DIAK[™] No. 7 will tend to increase mold fouling and sticking and should be avoided when possible.
- A general rule, to maximize processing performance, is that the coagent level used should be the minimum that is needed to give the required properties as any excess will generally deteriorate processing without bringing any additional advantages.

Physical Properties

The lower level of ionic end groups in the APA polymers helps contribute to the excellent flow characteristics and efficient curing chemistry of these new polymers. The APA polymers form less ionic interactions in the cured compound, leading to lower modulus and higher elongation compared with the older polymers. In high temperature tensile tests, these ionic interactions disappear from the older grades and the APA polymers have higher hot tear strength and modulus than their older counterparts.

This lowering of ionic interaction has beneficial features that should be taken into account when compounding and processing the APA polymers.

- The lower modulus and higher elongation of the APA polymers mean that these polymers can accept a higher filler level to provide the same compound hardness.

- The improved high temperature physical properties mean that the APA polymers demold better from complex shapes. This characteristic helps overcome mold sticking without part damage, i.e. they have higher cohesive strength to overcome adhesive forces.

Non-Black Fillers

The lower level of ionic end groups in the APA polymers also lowers the polymer-filler interactions between these polymers and certain mineral fillers.

- Lower, but acceptable, tensile strengths have been observed when using untreated fillers such as Blanc Fixe[®] (BaSO₄), Albaglos[®] (CaCO₃) and Nyad[®] (Calcium Metasilicate) compared with similar compounds made with the older peroxide cured grades.
- Tensile strengths with treated fillers such as 10 Wollastocoat[®] 10022 (or Tremin[®] 283 600 EST) provide generally higher mechanical properties and are the preferred mineral fillers.
- Surface treated fillers also provide improved molding characteristics and are less sensitive to moisture.
- This decrease of tensile strength with untreated fillers is more pronounced with the LT types (GLT-S, GBLT-S and GFLT-S) and the use of treated fillers in non-black LT formulations is recommended.
- Examples of treated calcium metasilicate fillers that work well with peroxide cured Viton[®] include Wollastocoat[®] 10022 (methacrylate treated), Wollastocoat[®] 10014 (vinyl silane treated), and Wollastocoat[®] 10012 (amino silane treated).

Additional detailed information can be found in the product data sheets of the 65 Mooney peroxide cured types. Filler studies are included with three levels of MT Black (N990) and two to three mineral fillers

Process Aids

The mold flow, mold sticking and mold fouling characteristics of the APA polymers are much improved over the previous generation of peroxide cured Viton[®] products. Thus lower levels of process aids are needed to take advantage of the outstanding processability of these new polymers. Since certain process aids can have a negative impact on tensile properties and compression set resistance, particularly when used at higher levels, using lower levels is good practice. It is generally true that the best results, in terms of mold flow and release, are obtained when using a package consisting of two or three chemically different process aids.

- Armeen[®] 18D is very effective as a release agent but should be used only at low levels. If used at levels above 0.5 phr Armeen[®] 18D has been shown to have a significant negative impact on tensile strength and compression set resistance.
- Struktol[®] WS-280 is a product that assists flow considerably without any significant negative impact to vulcanizate properties and may be used at higher levels.
- Waxes like carnauba and VPA No.2 are effective as release agents and assist in flow but they should also be kept to a relatively low level to avoid deterioration of properties.
- PAT 777 has been shown to function very well, both as a release agent to help flow, and does not appear to impact properties as much as waxes.
- Recent trials with Struktol[®] HT-290 have indicated it to be an excellent all round process aid, providing good mold release with a substantial improvement in flow.

A typical starting process aid package for black filled peroxide cured fluoroelastomers was a mixture of Armeen[®] 18D (0.2 to 0.4 phr), wax (0.3 to 0.5 phr) and Struktol[®] WS-280 (0.5 to 0.8 phr). Recent tests have shown that a mixture of PAT 777 (up to 0.5 phr) and Struktol[®] HT-290 (0.5 to 0.75 phr) provide provides far superior performance. Sometimes it may help to add a low level of wax like carnauba or VPA #2 to this mixture (0.2 to 0.4 phr). Testing has shown that the most effective single process aid for APA polymers is Struktol[®] HT-290, used at around 1 phr if it is the only process aid in the recipe. Carnauba wax or VPA #2 are effective process aids for mill, calender, and extrusion release and smoothness. The optimal level of wax (or other migratory process aid) will depend to a large extent on the filler level and on the mold geometry but levels as low as 0.2 to 0.3 phr can have a significant beneficial effect. For mineral filled compounds the same process aids work well but the levels may need to be increased. Since the capacity of mineral fillers to retain process aids varies with filler type and surface treatment it is difficult to give optimal levels. A general rule is that compounds using primarily untreated mineral fillers will need higher levels of process aid.

For additional detailed information Table 3 in the Viton® GBL-600S product data sheet presents a study comparing compounds with no process aid, 0.5 phr of Armeen® 18D, 0.5 phr Struktol® WS-280, 1 phr carnauba wax, and combinations of Armeen® 18D with Struktol® WS-280.

Metal Oxides

The lower level of ionic end groups coupled with the improved cure site chemistry results in less dependence on the metal oxide for efficient curing. Thus metal oxide type and level is less critical in the APA polymers than in their older peroxide cured counterparts.

- Zinc oxide is still the metal oxide of choice for the best long term and high temperature heat aging but calcium hydroxide, magnesium oxide or hydrotalcite can be used for special applications where needs such as metal bonding dictate.
- The standard level of metal oxide is 3 parts, however APA polymers with lower levels of metal oxide, or even no metal oxide, can be used provided a modest loss in heat resistance is not a issue.

For additional detailed information, Table 3 in the VTR-8550 (GFLT-S) product data sheet, presents a metal oxide study comparing zinc oxide to magnesium oxide, calcium hydroxide, and calcium oxide in addition to a zinc oxide/magnesium oxide blend which may be useful for metal adhesion with good heat aging.

Mixing the New Peroxide Curable Polymers

General

The new Viton® fluoroelastomer polymers made using Advanced Polymer Architecture technology are very different in terms of rheological properties compared to the older types of peroxide cure Viton® products. The differences are mainly due to the molecular weight distributions, cure site monomers and end group configurations of the new polymers. The new product compositions have been optimised to give excellent processability in terms of extrusion, mold flow and demolding characteristics and one consequence is that they have significantly less nerve than their old counterparts and need to be handled accordingly when mixing.

It can generally be said that :

- GF-600S (VTR-8600) will handle more like Viton® GF-300 than Viton® GF
- GBL-600S (VTR-8650) will handle more like Viton® GBL-200 than Viton® GBL-900
- VTR-8500 (65 Mooney GLT-S) will handle more like Viton® GLT-305 than Viton® GLT
- VTR-8525 (65 Mooney GBLT-S) will handle more like Viton® GBLT-301 than Viton® GBLT-601
- VTR-8550 (65 Mooney GFLT-S) will handle more like Viton® GFLT-300 than Viton® GFLT

A general rule is that the new polymers require some heat input early in the mixing cycle to allow the formation of a good band (mill mixing) or to allow the rotors to grab (internal mixing).

Mill Mixing of New Peroxide Curable Polymers

Because of their different molecular structure and end group configurations the new polymers tend to be drier during mixing than their old counterparts and in order to easily form a rolling band it is required to generate some heat. Specific mixing cycles will vary depending on batch size and mixer type but some general advice on procedure is as follows :

- Do not use excessive cooling on the mill rolls as this will inhibit the generation of heat and make formation of a band more difficult.
- Use a standard friction ratio of around 1.2:1 to 1.3:1
- Start the mix with a relatively tight nip, warming the polymer by passing it through the rolls until it starts to adhere and form the initial band. – Note that if the nip is too wide the polymer may become lacy and bag on the rolls, making formation of a band very difficult.
- Once the initial band is formed the mix can proceed as normal, progressively adding ingredients and opening the nip as the compound volume increases. Premixing the dry ingredients together, then adding them as one item can help the incorporation time.

- Liquid ingredients like DIAK™ 7 are best pre-mixed with some filler to form a paste before adding incrementally. Adding too much liquid or paste at one time always results in difficult mixing, regardless of polymer type. Adding DIAK™ 7 and peroxide too rapidly can cause the batch to be “baggy” on the mill.
- Once mixing is complete the usual rules regarding refinement of the compounds apply.

Internal Mixing of New Peroxide Curable Polymers

Internal mixers come in various sizes and designs so it is difficult to define a “universal” mixing procedure. In general, however, it is important to induce some heat early in the mixing cycle to induce the rotors to grab the mix. Some general advice is as follows:

- Do not use excessive cooling on the mixer as this will inhibit the generation of heat and make it more difficult for the rotors to grab the mix.
- A standard “right side up” mix procedure with the polymer first then the filler mix is recommended.
- Use a relatively high load factor. A minimum load factor of 72% is recommended. If the load factor is too low the mix will not incorporate and the result will be powder. Note that the load factor for the new polymers **MUST BE HIGHER** than for the old product line. Mixes that have gone to powder can often be recovered by adding additional polymer or compound (seeding).
- In some cases it may be useful to premix the polymer (for around 30 seconds with the ram down) prior to adding the other ingredients as this will generate the required heat.
- Upside down or sandwich type mixes are not preferred since the objective is to induce heat into the polymer prior to adding the other ingredients. Incorporation of process aids should be done late in the mix cycle and possibly with a split addition to avoid loss of torque in the mixer

Processing the New Peroxide Curable Polymers

Cure Rate

Cure rates of the APA polymers are significantly faster than those of comparable compounds made with the older peroxide cured polymers.

- Cure onset times (ODR ts2 and MDR ts1) are correspondingly shorter as well.
- These times can be extended in critical applications by using the slower peroxide, such as Varox® DBPH50-HP or Varox® 130XL, or by curing at a lower temperature.
- In some cases, the addition of 0.1 to 0.25 parts of a phenolic antioxidant (example: BHT) will extend the onset times without significant deterioration in cure rate or state, providing there is sufficient peroxide in the compound.

If an antioxidant is to be used as a scorch retarder then the level of peroxide may need to be increased marginally. The antioxidant provides an improvement in scorch safety by consuming radicals so not all of the peroxide in the recipe is available for cross-linking. It is recommended, in the event that an antioxidant is used, that the minimum peroxide level be 1.5 phr (of the Varox® DBPH50 variety)

Post Cure

The curing efficiency of the APA polymers is such that good physical properties and excellent compression set resistance can be obtained without postcuring the polymers. Postcuring will increase tensile strength and lower elongation and thus may be required to meet demanding physical property specifications. Post curing also eliminates residual volatiles and can give better dimensional consistency in molded parts.

- The optimum postcure time for the APA polymers for static sealing applications is of the order of 2 to 4 hours at 232°C for black filled recipes.
- For mineral filled recipes longer post cure times are needed to fully develop physical properties. A post cure of 8-16 hrs at 232°C is recommended in the case of mineral filled compounds.
- For dynamic applications it may be necessary to use a 4 to 8 hour post cure even for black filled recipes to optimise wear resistance.

For additional detailed information the VTR-8550 (GFLT-S) product data sheet shows the effects of postcure time (0, 2 and 4 hr) in MT Black filled stocks in Table 3.

Mold Flow and Extrusion

Because of their low ionic end groups and tailored polymer morphology, the APA polymers have excellent mold flow characteristics. This allows the polymers to be used in compression and injection molding as well as extrusion compounds. Flow is influenced strongly by the choice of filler and process aids (see p. 3). When carbon black is selected compounds based on 65 Mooney polymer grades will give very good performance. For mineral filled compounds, it may be necessary to blend high and low Mooney polymer grades to achieve a suitable viscosity, particularly in the case of very high shear processes like transfer and cold runner injection molding.

Mold Release and Fouling

The APA polymers have excellent mold release and low mold fouling properties and require minimal process aids. Best results are achieved with chrome-plated molds in good condition. Worn plating can lead to increased sticking.

Appendix

List of Proprietary Chemicals & Ingredients

Sources of compounding ingredients used in this bulletin are listed here. This is not to imply that comparable ingredients from other sources might not be equally usable.

<u>Material</u>	<u>Composition</u>	<u>Supplier</u>
Albaglos® ¹	Calcium carbonate (precipitated)	Specialty Minerals, Inc New York, NY 10174-1901
Armeen® 18D ²	1-Octadecanamine, N-Octadecyl	Akzo Nobel Polymer Chemicals L.L.C Chicago, IL 60606
Blanc Fixe	Barium Sulfate (precipitated)	Whittaker, Clark, & Daniels South Plainfield, NJ 07080
Carnauba wax	carnauba wax	Frank B. Ross Co., Inc Jersey City, NJ 07304
DIAK™ 7	TAIC – triallyl isocyanurate	DuPont Dow Elastomers Wilmington, DE 19809
DIAK™ 8	TMAIC - trimethyllyl isocyanurate	DuPont Dow Elastomers Wilmington, DE 19809
Luperco® 101XL45 ³	45% active dispersion of 2,5-dimethyl-2-5-Di- (t-butyl-peroxy)hexyne-3	Atofina Chemicals, Inc. Philadelphia, PA 19103
Nyad® 400 ⁴	Calcium metasilicate	Nyco Minerals, Inc Willsboro, NY 12996-0368
PAT 777	Fatty acid derivative / wax	IDE Processes International Sales LLC – Kew Gardens, NY 11415
Struktol® HT-290 ⁵	Blend of fatty acid derivatives	Struktol® Co. of America Stow, OH 44224-0649
Struktol® WS-280	Silicone-organic compounds	Struktol® Co. of America Stow, OH 44224-0649
Tremin® 283 600EST		
Trigonox® 145 45B ²	45% active dispersion of 2,5- dimethyl-2-5-Di-(t-butyl-peroxy) hexyne-3	Akzo Nobel Polymer Chemicals L.L.C Chicago, IL 60606
Varox® 130XL ⁶	45% active dispersion of 2,5- dimethyl-2-5-Di-(t-butyl-peroxy) hexyne-3	R.T. Vanderbilt Co. Norwalk, CT 06855
Varox® 802-40KE ⁶	40% active dispersion of alpha -alpha'-Di(t-butylperoxy)- diisopropylbenzene	R.T. Vanderbilt Co Norwalk, CT 06855

Varox [®] DBPH50 ⁶	45% active dispersion of 2,5-dimethyl-2-5-Di-(t-butyl-peroxy) hexane	R.T. Vanderbilt Co Norwalk, CT 06855
Varox [®] DBPH50-HP ⁶	45% active dispersion of 2,5-dimethyl-2-5-Di-(t-butyl-peroxy) hexane with an additive	R.T. Vanderbilt Co Norwalk, CT 06855
Varox [®] DCP-40KE ⁶	40% active dispersion of Dicumyl Peroxide	R.T. Vanderbilt Co Norwalk, CT 06855
Viton [®] fluoroelastomer	Fluorinated synthetic rubber (FKM)	DuPont Dow Elastomers Wilmington, DE 19809
VPA No. 2	Ricebran wax	DuPont Dow Elastomers Wilmington, DE 19809
Wollastocoat [®] 10022 ⁴	Calcium metasilicate (treated)	Nyco Minerals, Inc Willsboro, NY 12996-0368
Wollastocoat [®] 10014		
Wollastocoat [®] 10012		

¹Trademark of Pfizer Corporation

²Trademark of Akzo Nobel Polymer Chemicals L.L.C

³Trademark of Atofina Chemicals, Inc.

⁴Trademark of Nyco Minerals, Inc

⁵Trademark of Struktol[®] Co.of America.

⁶Trademark of R.T. Vanderbilt Co.

NOTES:

For more information on Viton® or other elastomers, please contact one of the offices below, or visit www.dupont-dow.com/viton.

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