DuPont™ Vamac® Ethylene Acrylic Elastomer

Improved Low Temperature Compounds

Technical information – December 2013

Summary

Three factors have led to the improvement of low temperature properties for compounds based on Vamac®. These include a combination of

1. Low temperature polymer (VMX 4017)
2. High viscosity Vamac® polymer (Ultra IP)
3. Low volatility plasticizer

Compounds using these three ingredients have good low temperature properties both before and after heat and fluid aging. Two key low temperature properties are

- Compound Tg's (glass transition temperature) as low as -50 °C
- TR10 (Temperature of retraction – 10%) values as low as -43 °C

These compounds also maintain the expected properties of a Vamac® compound including good fluid resistance, good heat resistance, good dynamic properties and good processability.

"Standard" Low Temp Vamac® Compounds

The traditional way to improve the low temperature properties of Vamac® compounds has been to start with Vamac® G and add high levels of plasticizers. These compounds have good initial low temperature properties and they can meet the end use requirements.

However, the compounds are difficult to mix and to mold because they are relatively low in viscosity and they are also "tacky". Also, as these compounds undergo heat aging in air at elevated temperatures they lose most of their plasticizer due to volatization. This can be shown by measuring the weight loss during aging and also by measuring the increase in the Tg after heat aging. The weight loss for compounds with the standard plasticizer is relatively high and the heat aged Tg approaches the Tg of a control compound with no plasticizer.

The combination of processing problems and poor low temperature properties after heat aging has made it difficult to use compounds made based on Vamac® G in applications that need outstanding low temperature properties.

VMX 4017

VMX 4017 is a developmental ethylene acrylate copolymer from DuPont that uses an acidic cure site monomer so compounds can be cured with diamines. The key attribute of the polymer is that it has a Tg of -42°C which is about 10°C lower than Vamac® G. This translates into a VMX 4017 compound that has a Tg that is about 10°C lower than a comparable Vamac® G compound. Compounds made from

VMX 4017 have similar heat resistance, compression set and CSR (compressive stress relaxation) properties when compared to a compound made from Vamac® G.

There are always trade-offs in elastomer compounds. The compounds using the VMX 4017 have constraints around fluid resistance and processing.

- The fluid resistance is not as good as the G compounds. For example a 70 Shore A VMX 4017 compound with no plasticizer will have a VI (volume increase) of around 27% in synthetic engine oil like Mobil 1 5W30 and around 80% in IRM 903 (after aging for one week at 150C).
- The VMX 4017 compounds are not easy to mix and mold because they are low in viscosity and they are relatively “tacky”.

Low Volatility Plasticizers

Several plasticizer suppliers have introduced polyether/ester plasticizers that have good low temperature properties along with lower volatility compared to the standard plasticizers used in compounds based on Vamac®. Compounds made with these low volatility plasticizers have good initial low temperature properties and they maintain these low temperature properties after aging in air for one week at 175 °C or for six weeks at 150 °C.

When used in combination with VMX 4017 they improve the low temperature performance of the compounds by up to 8°C. The Tg of a VMX 4017 compound with 15 phr of the plasticizer can be as low as -50°C and the TR10 can be as low as -43 °C.

An added benefit of the plasticizers is that they can improve the fluid resistance. A 70 Shore A VMX 4017 compound with 15 phr plasticizer will have a VI in Mobil1 5W30 of about 19% and a VI in IRM 903 of about 68%.

The low volatility plasticizer improves the low temperature properties and the fluid resistance but it does not improve the processing problems of the VMX 4017 compounds. It actually makes the processing more difficult because it lowers the compound viscosity and it increases the “tackiness”.

Vamac® Ultra IP

Vamac® Ultra IP is an improved processing (IP) version of Vamac® G. It has a Mooney Viscosity of 29 compared to Vamac® G at 16 and VMX 4017 at 11 (ML (1+4) @ 100 °C).

A combination of Vamac® Ultra IP and VMX 4017 can be used to improve the processability of a compound based only on VMX 4017. The compound viscosity will increase and the compound will become less “tacky”.

The addition of Ultra IP will also improve the fluid resistance. A 70 Shore A compound that uses 50 phr Ultra IP, 50 phr VMX 4017 and 15 phr plasticizer will have a VI in Mobil 1 5W30 of 13% and a VI in IRM 903 of 58%.

The Ultra IP polymer has a Tg of about -32°C so it will increase the Tg of a compound based on VMX 4017. The compound mentioned above – a 50/50 blend of VMX 4017 and Ultra IP along with 15 phr of plasticizer – has a Tg of about -47°C. This is still a very good low temperature compound.

The Vamac® Ultra IP also has improved dynamic properties compared to Vamac® G and this will be discussed later.

Low Temp after Fluid and Heat Aging

The low temperature properties of compounds based on VMX 4017 and Vamac® Ultra IP were measured initially and also after aging in air and aging in fluids. These compounds have very good low temperature properties after going through both aging processes. They are significantly better than Vamac® G compounds.

An interesting observation was seen with compounds that had plasticizer levels that varied from 0 to 30 phr. As expected there was a large difference in the initial Tg values. After fluid aging all of the compounds had Tg values that were very close – and were similar to a compound with about 15 phr plasticizer. The compounds with no plasticizer had a significant <u>decrease</u> in Tg after fluid aging while the compounds with 30 phr plasticizer had a significant <u>increase</u> in Tg after fluid aging. The compounds with 15 phr plasticizer had little or no change in Tg after fluid aging.

Most of the compounds discussed in this bulletin use either 0 or 15 phr plasticizer.

Major Performance Properties and Applications

Cured compounds made from VMX 4017, Ultra IP and a low volatility plasticizer have a good combination of properties including a wide operating window for end use temperatures that ranges from -50 °C up to 175°C. The compounds can withstand short term temperature spikes up to 200 °C.

The cured compounds are typically rated as class E for heat resistance using the ASTM D2000 system and this means that they will pass a heat rating test of 70 hours at 175 °C (347 °F).

The fluid resistance of a cured compound depends on the formulation used. Some key factors are the level of each polymer, the plasticizer and carbon black levels and the cure package. Typical values for volume swell in IRM 903 fluid after aging for 168 hours at 150 °C (302°F) ranges from 60 to 80%. This means that the compounds are rated as Type E using ASTM D2000. Some of the compounds are between 40 and 60% swell in IRM 903 and they are rated as Type F.

IRM 903 is a standard reference fluid with a relatively high aromatic content. It is much more aggressive to Vamac® compounds compared to transmission fluids, engine oils and high temperature greases. This means that the VI in IRM 903 may not be a good predictor of how a compound performs in the actual end use fluid. For comparison – the volume swell for these new compounds ranges from about 13 to 27% in Mobil 1 5W30 (after one week/ 150 °C) and from about 30 to 45% in SF105.

The compression set values for compounds based on VMX 4017, Ultra IP and the low volatility plasticizer were measured after 70 hours at 150 °C using the ASTM plied method as well as the ISO molded buttons. The comp set values ranged from 15 to 30% and the results followed the usual trends. The comp set improved as the curative level increased and when the plasticizer levels decreased.

CSR tests run on VMX 4017 compounds with plasticizer and the compounds show very good properties for six weeks at 150 °C in engine oils. The percent retained sealing force is a relatively high value and this is probably due to the relatively high volume swell. The VMX 4017 compounds have higher values compared to the Vamac® G compounds which in turn have higher retained sealing forces compared to Vamac® GLS compounds.

It is not easy to measure dynamic properties of elastomeric compounds with a simple test that predicts good end use performance. The end use requirements vary considerably from end use to end use – factors such as temperature (both high and low), frequency and strain rate all play a part in end use performance.

The DeMattia flex test was used to study the dynamic properties of the compounds based on VMX 4017. The test was run on non-pierced samples at 150°C (ASTM D430, ISO 132) and on pierced samples at 23°C (ASTM D813, ISO 133). The trends seen with these compounds were comparable to other studies with Vamac® compounds. The compounds had better flex properties when the hardness was lowered and when the compression set was higher (milder cure package).

The two trends that favor better dynamic properties – lower hardness and a milder cure package – also lead to higher volume swell in fluids. One needs to balance the compound properties to meet all of the end use requirements.

The properties of compounds based on VMX 4017, Vamac® Ultra IP and a low volatility plasticizer make them useful for a wide range of automotive applications. Some of these are molded boots, powertrain seals and gaskets, rocker cover seals, transmission oil coolant hoses, power steering hoses, turbocharger hoses, crankcase ventilating tubes, coverings for fuel and coolant hoses, O-rings, grommets and crankshaft dampers.

These compounds are halogen free and thus can be used for flame retardant, low-smoke, non-halogen wire and cable jackets and in non-halogen, low smoke flooring.

VMX 4017 compounds are well suited for injection, transfer or compression molding. They also can be extruded.

Handling Precautions for VMX 4017

VMX 4017 contains small amounts of residual methyl acrylate monomer and residual n-butyl acrylate monomer so adequate ventilation should be provided during mixing and processing to prevent worker exposure to the acrylate monomers. Additional information may be obtained in the Vamac® VMX 4017 Material Safety Data Sheet (MSDS) and the bulletin "Safe Handling and Processing of Vamac® and Compounds Made from Vamac®" (VME-A10628-00-D0212). Both are available from the DuPont Performance Polymers sales office serving you. The MSD sheet is also available at the following web site, vamac.dupont.com

Product Properties of VMX 4017

Property	Target Values	Method
Mooney Viscosity, ML (1+4) at 100°C (212°F)	11	ASTM D 1646
Total Volatile Matter (weight percent)	≤ 0.6	Internal DuPont Test
Form	Bale Size is nominally: 560 mm by 370 mm by 165 mm (22x15x7 inches)	Visual inspection
Color	Clear to light yellow translucent	Visual Inspection

Compound and Vulcanizate Properties based on VMX 4017, Ultra IP and Low Volatility Plasticizers – compared to Vamac® G

The following table shows the formulation for six different compounds along with some of the predicted properties. The first two compounds are control compounds based on Vamac® G. The first compound has no plasticizer and the second one has 15 phr of a "standard" plasticizer. The next two compounds are based on VMX 4017 where one compound has no plasticizer and the other has 15 phr of a low volatility plasticizer. The last two compounds are based on 50/50 blends of VMX 4017 and Vamac® Ultra IP and they have 0 or 15 phr of a low volatility plasticizer. The compound formulations also include 1.5 phr Stearic acid, 1.0 phr Vanfre® VAM, 0.5 phr Armeen® 18D and 2 phr Naugard® 445.

Extensive DOE's (Design of Experiment) have been run on these compounds and models have been developed to predict the properties. The black level in the models was adjusted to give a hardness of about 70 Shore A so that the compounds could be compared at equal hardness values. The cure conditions used in the modeling work included a 10 minute press cure at 180°C followed by a four hour post cure at 175°C. The formulations, predicted Mooney Viscosity and the predicted initial cured physicals are shown in the first table. The predicted initial low temperature properties are included and the compounds with the VMX 4017 have the best low temperature properties.

	G control with no plasticizer	G control with 15 phr std plast	VMX 4017 with no plasticizer	VMX 4017 with 15 phr low vol plast	50/50 IP/ 4017 with no plasticizer	50/50 IP/ 4017 with 15 phr low vol plast
VMX 4017			100	100	50	50
Vamac® Ultra IP					50	50
Vamac® G	100	100				
"standard" plasticizer	0	15				
Low Volatility plast			0	15	0	15
N550	**48**	**68**	**52**	**63**	**49**	**60**
Diak™ #1 (HMDC)	1.5	1.5	1.5	1.5	1.5	1.5
Vulcofac® ACT 55 (DBU)	2	2	2	2	2	2
Mooney Viscosity						
ML(1+4)@100	57	41	47	**32**	58	39
Hardness, Shore A	**70**	**70**	**70**	**70**	**70**	**70**
M100, Mpa	6.0	5.6	6.2	6.1	6.2	6.1
Tensile, Mpa	19	14	16	13	19	16
% Elongation	251	243	215	192	249	222
Tg by DSC, Initial, °C	-29	-39	-44	**-50**	-40	**-47**
TR 10, °C	-28	-32	-37	**-43**	-30	**-36**

The compounds based on VMX 4017 have lower viscosities than the Vamac® G controls and lower tensile and elongation values. The 50/50 blends of VMX 4017 and Vamac® Ultra IP have similar viscosities and similar physicals to the Vamac® G controls.

The low temperature properties improve as the plasticizer level is increased and also as more VMX 4017 is used. The best low temperatures are seen in compound 4 which has all VMX 4017 and 15 phr of plasticizer.

Compression Set

The predicted compression values of the compounds are shown below. All of the compounds have good compression set values. The G control compound with the standard plasticizer has the highest compression set.

Comp Set -- 70 hour/150 ˚C						
	G control with no plasticizer	G control with 15 phr std plast	VMX 4017 with no plasticizer	VMX 4017 with 15 phr low vol plast	50/50 IP/ 4017 with no plasticizer	50/50 IP/ 4017 with 15 phr low vol plast
ISO molded buttons	15	**27**	17	21	16	20
ASTM plied buttons	13	**24**	14	17	13	15

Fluid Aging

The compounds were fluid aged for one week at 150 ˚C in three different fluids. The predicted VI results for each fluid are shown below. As expected the VMX 4017 compound with no plasticizer has the highest VI values. The 50/50 blend of VMX 4017/Ultra IP with 15 phr plasticizer has relatively good fluid resistance. The VI results in IRM 903 are much higher than the engine oils. It is important to run the fluid aging tests in the actual fluid used in the end use application.

Fluid Resistance -- VI -- after 1 week at 150 ˚C						
	G control with no plasticizer	G control with 15 phr std plast	VMX 4017 with no plasticizer	VMX 4017 with 15 phr low vol plast	50/50 IP/ 4017 with no plasticizer	50/50 IP/ 4017 with 15 phr low vol plast
Mobil 1 5W30	19	12	27	19	21	13
SF 105	27	21	46	37	36	29
IRM 903	55	48	**80**	68	68	58

Low Temperature Properties after air aging and after fluid aging

Low temperature properties are typically measured only on the initial cured compounds. For the DOE model used in this study the Tg by DSC was also measured after aging in air for one week at 175 °C as well as after aging in IRM 903 for one week at 150 °C.

The G compound with the standard plasticizer had the largest predicted increase in Tg after air aging – the Tg increased by 9 °C. This is mainly due to the use of the “standard” plasticizer. This compound had the highest weight loss during aging which reflects the loss of plasticizer. The compounds with no plasticizer or with the low volatility plasticizer had an increase in Tg of only one to three °C after heat aging.

The compounds based on VMX 4017 or VMX 4017/Ultra IP had very good low temperature properties after fluid aging. The Tg values were about -50 °C. Both of the Vamac® G controls had Tg’s of about -40 °C after fluid aging.

To ensure good end use performance a suggestion is to measure the low temperature properties of the compounds after heat aging in air and fluid aging in the end use fluid.

Low Temperature Properties After Aging -- Tg by DSC						
	G control with no plasticizer	G control with 15 phr std plast	VMX 4017 with no plasticizer	VMX 4017 with 15 phr low vol plast	50/50 IP/ 4017 with no plasticizer	50/50 IP/ 4017 with 15 phr low vol plast
Initial	**-29**	-39	-44	-50	-40	-47
Air Aging -- 1 wk at 175C	**-26**	**-30**	-42	**-49**	-38	**-45**
1 wk in IRM 903 at 150C	**-39**	**-39**	-52	**-53**	-49	**-50**

Dynamic Properties

The typical way to improve the dynamic properties of a Vamac® compound is to go to a softer compound (lower hardness and/or modulus) and to a lower state of cure (higher compression set). These two methods were modeled for compounds based on blends of VMX 4017 and Ultra IP. There was a significant improvement in dynamic properties as measured by DeMattia flex. However, the drawback with these two changes is that both increase the VI values for fluid aging and both changes make it more difficult to process the compounds. One needs to balance the dynamic properties versus the fluid aging requirements and the processability requirements.

The following table shows three compounds that differ significantly in predicted DeMattia flex properties. The first column has a 70 Shore A hardness compound with a high state of cure (low comp set) while the last column has a 60 Shore A compound with a low state of cure (relatively high comp set). The compound in the last column has the best dynamic properties – but it also has the lowest viscosity and the highest VI numbers. The dynamic properties of the 60 Shore A compound are between 15x and 100x better than the 70 Shore A compound.

	70 Shore A with high state of cure	65 Shore A with intermediate state of cure	60 Shore A with low state of cure
VMX 4017	50	50	50
Vamac® Ultra IP	50	50	50
Low Volatility plast	15	15	15
N550	**60**	**54**	**48**
Diak™ #1 (HMDC)	**1.5**	**1.3**	**1.1**
Vulcofac® ACT 55 (DBU)	**2**	**1.5**	**1**
Mooney Visc - ML(1+4)@100	**39**	**33**	**29**
Hardness, Shore A	**70**	**65**	**60**
M100, Mpa	6.1	4.4	3.2
Tensile, Mpa	16	15	15
% Elongation	220	270	330
Tg by DSC, Initial, °C	-47	-46	-46
TR 10, °C	-36	-36	-36
Comp Set -- 70 hour/150C			
ISO molded buttons	20	23	27
ASTM plied buttons	15	16	18
VI after one week/150C			
Mobil 1 5W30	13	15	17
SF 105	29	32	35
IRM 903	58	64	72
DeMattia Results			
D813, pierced, RT			
Relative performance cycles to 8.5 mm cut length	**1**	**4**	**15**
D430, 150C			
Relative performance average cycles to failure	**1**	**11**	**120**

Compounds based on VMX 4017, Ultra IP and a low volatility plasticizer can be designed to meet compounds with outstanding low temperature properties. As with all elastomer compounds there will be trade-offs between end use performance requirements as well as processability. Please consult with your DuPont representative if you need help designing a compound.

Materials used in formulations and test fluids – General composition and Supplier

Material	Chemical Composition	Supplier
Polymer		
Vamac® G	Ethylene Acrylic Elastomer	DuPont
Vamac® Ultra IP	Ethylene Acrylic Elastomer	DuPont
VMX 4017	Ethylene Acrylic Elastomer	DuPont
Release Aids		
Armeen® 18D	Octadecyl Amine	Akzo Nobel
Vanfre® VAM	Complex Organic phosphate ester	R.T. Vanderbilt
Stearic Acid		
Anti-Oxidant		
Naugard® 445	Diphenyl Amine	Chemtura
Plasticizer		
TP-759	Mixed Ether/Ester Plasticizer	PlastHall
Tegmer® 812	Low Volatility Plasticizer	PlastHall
Fillers		
N550	Carbon Black	
Curatives		
Diak™ #1	Hexamethylene Diamine Carbamate	DuPont
Vulcofac® ACT 55	Heterocyclic Amine Accelerator	Chemspec
Test Fluids		
Mobil 1 5W30	Synthetic Engine Oil	ExxonMobil
IRM 903	Test Fluid	ASTM Test Monitoring Center
Service Fluid 105	Service Fluid 105	ASTM Test Monitoring Center

The ASTM test methods used in the work are shown below along with the comparable ISO method.

	ASTM method	Comparable ISO method
Rheology		
Mooney Viscosity	D 1646	289-1
Mooney Scorch	D 1646	289-2
MDR	D 5289	6502
Physicals		
Hardness	D 2240	7619-1
Tensile, Elongation, Modulus	D 412	37
Tear, Die C	D 624	34
Fluid Aging	D 471	1817
Compression Set, method B	D 395	815-1
Tg by DSC	D 3418	22768
Aging in Air	D 573	188
Temperature of Retraction	D 1329	2921
DeMattia – non pierced	D 430	132
DeMattia – pierced	D 813	133

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