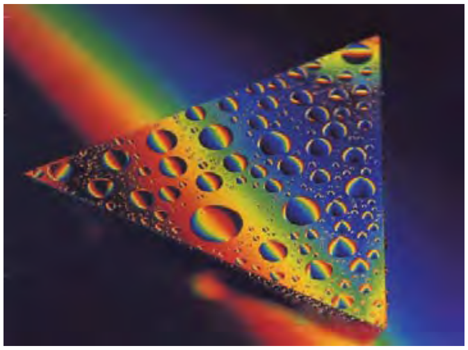

“The Reduction of Iridescence Bloom in Elastomeric Weather-stripping Application”

The Institute of Materials, Minerals & Mining

18th National Rubber Conference 2007
March 9, 2007
Eastern Cape, South Africa

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INTRODUCTION

Ethylene propylene elastomers continue to be used extensively by the automotive industry to produce both molded and extruded articles. Approximately 50% of the non-tire rubber used in a car is based on EPDM. This is attributed to the fact that they have fully saturated backbones, giving excellent resistance to oxygen and ozone. As non-polar hydrocarbon elastomers, they also have excellent electrical and low temperature flexibility with glass transition points of -60°C and higher. Current automotive applications include door, trunk, and window sealing, including fixed and movable glass. An average automobile uses approximately 11-16 kilograms of weather-stripping per car. The most current (2005) elastomers breakdown of weather-stripping used in the North American market is as follows:

Table I[1]

Sealing-Front and Rear	**Side Fixed Glass**	**Movable Glass**
90% EPDM	40% Polyurethane RIM	85% EPDM
10% TPE	30% PVC	15% TPE
	18% EPDM	
	12% TPE	


Sealing-Front


Side Fixed Glass

As a major component, both inside and outside of a car, EPDM weather-stripping esthetics play a large part of the overall quality that any customer perceives. In the mid 1980's, most of the weather-stripping in the USA was made from SBR. Unfortunately, SBR did not weather well, and failures of these units were common after four or five years. Then, under pressure to improve quality to compete with Japanese imports, the American car companies began to offer five-year warranties, and changes were needed to improve product reliability. These changes included switching from SBR to EPDM. Today the automotive industry expects "Show Room New" after a minimum of five years of service on these articles. The switch to EPDM immediately resolved the product reliability problem but, unfortunately, another problem called "iridescence" started to appear. The iridescence sheen phenomenon occurs particularly in EPDM when the fabricated articles are exposed to ultraviolet light (sunshine) and ozone. The sheen is a surface phenomenon, which exhibits visual colors of gold, greens and primary blues. The greater the surface area of the extruded or molded part, the more intense the condition of iridescent sheen.

Even though the sheen does not seem to affect the product reliability, its chromatic appearance has been found objectionable by the automotive industry. The oil on water appearance associated with the iridescent sheen phenomenon hinders broader use of EPDM in many automotive applications.

Oil on Water Appearance

This paper is a continuance of a paper presented at an American Chemical Society Rubber Division Meeting. It was presented in Orlando, Florida in September 1999. In this meeting we addressed the different issues relative to the iridescence phenomenon. We introduced a unique filler called "Neuburg Siliceous Earth", trade named Hoffmann Mineral Sillitin Z86, from Neuburg, Germany. This study provided compounders with key compounding suggestions that aided in the reduction of iridescence, improved profile esthetics, and increased plant productivity. In this paper we found that the black/non-black compounds outperformed the 100% black compound. Also, STRUKTOL® HM 97 proved to be superior to STRUKTOL® EF 44A in down line processing benefits. Note, STRUKTOL® EF 44A was specifically developed for use in highly load silica tire compounds.

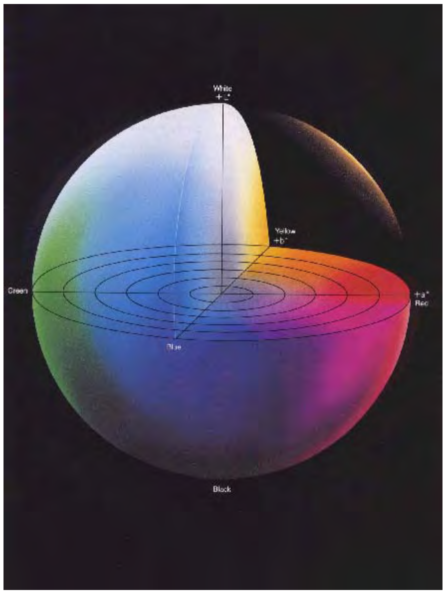
EXPERIMENTAL

Thanks to earlier work done by DSM (Europe) [2], Exxon Chemical Company[3], and Hoffmann Mineral[4], our systematic evaluation of the iridescence phenomenon was accelerated by starting our evaluation using the most current compounding techniques to reduce this annoying, unwanted bloom. The following list is all of the known and confirmed compounding practices used to reduce this bloom through 2006. It must be noted that this topic has been a pet project of mine ever since being employed as the technical manger of a large U.S. custom mixer in the late 1970's.

- The higher the unsaturation of the base polymer, the less tendency to become iridescent.
- Carbon black influences this phenomenon - replacing black with non-black fillers will reduce iridescence.
- Faster and higher curing temperatures reduce this problem.

- Diethylene and polyethylene glycol give a reduction in iridescence.
- T.M.Q, a common antioxidant, will reduce iridescence.
- Selecting oils low in residual sulfur will reduce iridescence.
- Selecting the appropriate cure system will reduce this bloom.
- Processing additives, which are only partially compatible with EPDM, will not reduce iridescence as was earlier believed. i.e. primary amides

Using all of the compounding techniques available, we started our initial trials using an optimized starting compound. Compounds were mixed, cured, and compression molded into standard EPDM tensile sheets. These rubber sheets were exposed to sunlight at our Stow, Ohio, facility. Other cured sheets were placed in a light proof box. After one month of sunlight aging, we used a Minolta Spectrophotometer, Model CM 508D, to quantitatively measure the differences in iridescence bloom between compounds. A spectrophotometer can accurately measure differences in hue, lightness and saturation, and express such differences exactly in numerical form (referred to as L*a*b*). The L*a*b* color space, or CIELAB, is presently one of the most popular ways to measure object color. In this color space, L* indicates lightness, and a* and b* are the chromaticity coordinates. For example, a human sees an apple as being red, but a spectrophotometer sees the red sample as a numerical value on a spectral graph. (L* 43.31, a* 47.63, b* 14.12).



Formulations Used in the 2006/2007 Study

In this study we replaced STRUKTOL® EF 44A with our newest additive, STRUKTOL® JV 46F and compared it to the proven winner of our 1999 study, STRUKTOL® HM 97.

Compound Ingredient Study

Table II

Formulations	**Experiment**			
	A	**B**	**C**	**D**
EPDM Keltan 40A (Low Diene 4.6%)	100.00	100.00	100.00	100.00
Paraffinic Oil (Sunpar 150)	45.00	45.00	45.00	45.00
Carbon Black N550	105.00	105.00	85.00	85.00
Sillitin Z 86	---	---	50.00	50.00
Stearic Acid	1.00	1.00	1.00	1.00
Zinc Oxide	5.00	5.00	5.00	5.00
DEG	3.00	3.00	3.00	3.00
Sulfur	1.50	1.50	1.50	1.50
MBT	1.50	1.50	1.50	1.50
TMTD	.50	.50	.50	.50
TBBS	.50	.50	.50	.50
ZDBC	1.50	1.50	1.50	1.50
DTDM	1.50	1.50	1.50	1.50
STRUKTOL® HM 97	2.00	0	2.00	0
STRUKTOL® JV 46F	0	2.00	0	2.00
Total	*268.00*	*268.00*	*298.00*	*298.00*

FIRST PASS MIX
ROTOR SPEED 77 FILL FACTOR 70%
0 SECONDS ADD EVERYTHING
90 SECONDS BRUSH AND SWEEP
120 SECONDS BRUSH AND SWEEP
240 SECONDS DISCHARGE

2^{ND} PASS MIX SPEC
ROTOR SPEED 77 FILL FACTOR 70%
0 SECONDS ADD ½ MB, CURES, AND ½ MB
30 SECONDS BRUSH AND SWEEP
212F OR 120 SECONDS DISCHARGE

Table III

Mooney Viscometer Test	**Experiment** **A**	**B**	**D**	**E**
Initial	95.0	92.5	78.0	70.9
ML 1+4	77.1	76.6	65.1	61.0
ODR Test				
180°C, 3° arc				
100 Rng, 12 min.				
Min. Torque	12.13	11.79	9.49	9.26
Max. Torque	98.71	91.07	95.50	93.48
T_2	.62	.62	0.70	.67
T_{50}	1.28	1.23	1.53	1.43
T_{90}	3.07	2.47	4.23	3.72

Table IV

Cure: 5 min. @ 180°C **Property Originals**	**Experiment** **A**	**B**	**C**	**D**
Hardness, Shore A	74	74	73	74
Tensile Strength, MPa	13.7	12.9	11.5	11.2
Elongation, %	277	289	299	295
Modulus 100%, MPa	6.1	5.1	4.9	5.0
Modulus 200%, MPa	11.6	10.2	8.4	8.3
Modulus 300%, MPa	------	------	-----	-----

Experiment

In this updated experiment, even though the lower the diene the less unsaturation and more iridescence, we used Keltan 40A with a diene value of 4.6%. In past experiments we found that diene values for EPDM in the 6% or higher range were far superior in lowering iridescence. In this experiment we mixed a total of four compounds, two compounds with 100% carbon black and two processing aids. For identity purposes, the additives used were STRUKTOL® JV 46F, a fatty acid derivative, and STRUKTOL® HM 97, a bi-modal polyethylene wax. The other two compounds that were mixed were a combination of carbon black and Neuburg siliceous earth, and the same additives. All compounds were mixed in a standard BR internal mixer. Rheological tests were run, and tensile sheets were cured 5 minutes at 180°C. Standard physical tests were run. After three weeks of outdoor aging, spectrophotometer measurements were taken of the aged and unaged sheets.

RESULTS AND DISCUSSIONS

Results of the Experiment

The goal of the experiments was to provide quantitative measurements of iridescence, and optimize towards the best compound. All mixed compounds provided expected end physical results. Interesting though, the two compounds using STRUKTOL® JV 46F provided further improvements in the reduction of the iridescence as measured by the highly accurate spectrophotometer, and further improvement in processability. Interpreting the spectrophotometers L*a*b* color space results on all samples was not only easy, but very reproducible. The L* value measures the lightness of the sample. As expected, the combination of black and non-black fillers produced higher L* values than the compounds with 100% carbon black. In the case of determining shades of iridescence, the b* value provided a direct correlation, the higher the negative value, the more bloom present, also confirmed visually. The results of our tests confirm the compounds using the Neuburg siliceous earth and carbon black provided lower values (less iridescence) than the compounds using 100% carbon black. All compounds were very close to being iridescence free. The compound using STRUKTOL® JV 46F provided improved results over the compounds using STRUKTOL® HM 97. It was also noted that STRUKTOL® JV 46F gave improved processing characteristics.

Table V
Sheets Cured 5 minutes at 180°C Light Proof 21 Days

Compound	**A**	**B**	**D**	**E**
L* value	18.8	16.8	23.0	20.6
a* value	-0.3	-0.1	-0.3	-0.1
b* value	-1.9	-1.7	-1.7	-1.6
Visual Appearance	slight	none	none	none

Table VI
Sheets Cured 5 minutes at 180°C Outdoor Aging 21 Days

Compound	**A**	**B**	**D**	**E**
L* value	18.8	16.6	21.5	20.6
a* value	-0.5	-0.4	-0.2	-0.3
b* value	-2.2	-1.8	-1.0	-1.8
Visual Appearance	slight	none	none	none

Table VII
Tear Strength ASTM D-624 Die C N/MM

Compound	23 °C
Compound A	33.6
Compound B	38.6
Compound C	27.9
Compound D	27.4

Table VIII
Spiral Mold Flow - Cured at 180°C

Compound	Cure	Weight 1	Weight 2	Weight 3	Average
Compound A	5	1.630	1.608	1.544	1.594
Compound B	5	1.859	1.816	1.756	1.810
Compound C	5	2.009	2.000	1.984	1.998
Compound D	5	2.065	2,087	2.017	2.056

Table IX Capillary Rheometer Data

Die L/D ratio: 15:1: 90 entrance angle: 1.5 mm orifice
70C, 180 sec preheat

	Apparent Stress (Pa)	Apparent Viscosity (Pa-s)	Apparent Stress (Pa)	Apparent Viscosity (Pa-s)	Apparent Stress (Pa)	Apparent Viscosity (Pa-s)	Apparent Stress (Pa)	Apparent Viscosity (Pa-s)
Shear Rate	**100/s**	**100/s**	**500/s**	**500/s**	**1000/s**	**1000/s**	**3500/s**	**3500/s**
Compound A	181,360	1574.3	253,420	506.87	336,470	336.45	434,170	125.63
Compound B	189,300	1543.2	260,750	501.53	308,990	308.97	445,160	128.81
Compound C	234,490	2035.5	292,500	585.04	346,240	346.22	453,100	131.11
Compound D	244,870	2025.6	302,270	564.58	353,570	353.55	456,770	132.17

Conclusions

Thanks to all earlier contributions, we started this project with a solid understanding of what compound ingredients could be used to reduce iridescence. We used a fully optimized cure system[3] and, in all compounds, iridescence was minimal. With the use of Sillitin Z86 and STRUKTOL® JV 46F, we were able to eliminate any signs of iridescence and produce a compound with enhanced flow properties, thereby improving in-plant processing. The final compound had a smooth, matte finish with a consistent, appealing surface.

For a shiny wet look, we suggest the introduction of primary amides into the compound. As the automotive industry continues to request improved aesthetics in their elastomeric parts, the rubber industry will continue to work to provide what is needed.

We found that the use of the spectrophotometer is a fast and effective tool to concisely measure iridescence.

The filler selection and EPDM characteristics are also key factors for improved results.

Processing additives can and will help both mixing and down line processing.

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4. Hoffmann Mineral, Non-black Fillers in EPDM (Sulfur Cured) (Hoffmann Mineral, Neuburg, Germany)