compounding colored rubber articles

Depth and Understanding: Coloring rubber can be a complicated and sometimes difficult task. This article will present ways to avoid problems in your base compound. But this is only half the battle. Selecting the proper colors for best match, weatherability, FDA needs, curing parameters, etc. is best done by color technologists. Let Akrochem help you with your coloring choices.

Color is an integral part of Akrochem's business. We asked ourselves how we could discuss color with our customers in such a way that it would be most useful to them. There are many technical presentations on the color pigments that are used in the rubber industry. These technical overviews are a wealth of information about different colorants but there are few rubber compounders that want to become color pigment experts. Most would like to just get their neutral rubber stock pigmented to a desired color without delving into the colorant chemistry.

If you, as a rubber compounder, wish to learn more about a pigment or pigments, please call our technical department to discuss specifics. In this way you will retain the information much better than if we inundated you with technical jargon. For that reason this presentation will primarily address the best ways to compound rubber to be colored. Once you have a base compound that meets your specs, we suggest you use Akrochem's color matching expertise to get the color you want.

Akrochem can take your neutral masterbatch (meaning everything is in the compound except colors) and color match it to almost any color. One easy way to discuss color with us or your customer is by using Pantone color standards (available from any local art store). But we've also matched to many other color "standards": paper, plastic, competitor's rubber, cloth; whatever has the color you need. We have a much better chance of finding the correct pigment that matches most closely to your control because Akrochem has a wide palette of colors from which to choose. Plus we can evaluate your need for weather and heat resistant pigments, as well as FDA requirements. This allows you to concentrate on the compound, not worry about color matching.

DESIGNING A COMPOUND:

Most rubber compounders are more concerned with a part's functionality and cost than they are with its appearance. The "look" of a part is seldom an issue in black parts (although bloom, iridescence and fingerprint-marking are less and less tolerated by customers). For colored rubber compounds it is often wise to pay attention to the color details that are desired in the part:

- Will the color(s) need to be bright and clean-looking? The best color comes from clean fillers (which are typically more expensive). Cheap fillers can be made into fairly bright colors by using a lot of titanium dioxide (TiO_2) and higher colorant levels (often resulting in a more expensive color overall).
- Will the color have to be consistent from batch-to-batch or is some color variation acceptable? The answer here will be crucial to raw material selection, where the stock should be mixed, and how much colorant (including TiO_2) needs to be added. Typically the more color added to a compound, the less batch-to-batch variation there will be.

- Will the compound be used for a single color for one part or will it be a neutral compound that will have different colors added to it? With a single colored part you may choose lower cost fillers even though coloring might be more difficult. A neutral to which you will add colors should be made more consistent by using more readily colored fillers.
- Will the part be exposed to sunlight? Continuously or sporadically? For long-term outdoor exposure, durable colorants must be used. Inorganics like iron oxides are the best but only dull colors can be achieved. Other inorganics like chromes and cadmiums can be used for brighter, durable colors but most facilities avoid these types of heavy metals. Organic pigments will provide the bright colors, but careful selection must be used for outdoor durability. To put it very briefly, outdoor durable blues, greens, white and off-white, tans and browns can be made with standard rubber colors while most other colors will require "high performance" (high performance usually translates to higher cost) pigments to be really durable outdoors.

polymer choice

ESPECIALLY FOR OUTDOORS

Elastomers cannot be easily protected from ultraviolet (UV) crazing (the excessive crosslinking of the exposed rubber surface that results in cracking and eventually a white dust that looks like a bloom. This "bloom" is actually the fillers left behind after the rubber has degraded). Ozone is a completely different mechanism of rubber destruction, so antiozonants have little or no effect against UV. While carbon black protects black rubber against UV degradation, only moderate UV protection can be gained in colored unsaturated elastomers by using high loadings of ZnO or TiO_2. Of course, this can make coloring the compound expensive and the specific gravity high.

For good polymer durability outdoors, EPDM is the preferred polymer (other saturated polymers like CSM, CPE, AEM, or EVA can also be used among moderately priced elastomers). Even EPDM should be specially compounded when exposed to extensive sunlight: only paraffinic oil should be used and those paraffinic oils with the lowest (or no) aromatic content are preferred; TiO_2 levels should be kept high. Only in the case of dark colors should the TiO_2 level be reduced when outdoor durability is the main criteria.

Finally, another misconception is that UV inhibitors will afford some protection to the rubber or to the colors. UV inhibitors work only if the light reaches them. In a typical opaque (no light passes through) rubber compound, light goes no further than the surface of the part. The only help from a UV inhibitor comes from the little bit on the surface of a cured part; most of the inhibitor is buried in the compound.

It should go without saying that for any colored rubber the cleaner polymers make better colors. Natural rubber technically specified for low dirt content makes good clean colors. To repeat a constant theme, you can use lower cost, dirtier natural rubber but coloring will be more difficult and more expensive. Synthetic elastomers for the most part are reasonably clean or at least have little color value (always use polymers with non-staining stabilizers and non-aromatic oil extension). The slight shade variation in some polymers will have minimal effect on the final color. However, there may exist substantial differences in color between different manufacturers. One example is Zeon's Zetpol (hydrogenated NBR). The manufacturing method results in a very dark elastomer that can be very difficult to compound into light, bright colors. For a bright HNBR, we would suggest using Bayer's Therban polymers that are more neutral in color.

Polychloroprene (CR) - is very prone to yellowing upon cure and is also susceptible to darkening upon sunlight exposure. High loadings of TiO_2 must be used in polychloroprene to develop any light colors. To demonstrate this, two compounds were made: one with sulfur modified polychloroprene ("G"-type); the other with a nitrile-PVC blend. Formulations were kept as similar as possible (see appendix). One phr of blue was added to each. The resulting cured colors are shown in *Display 1*. The sulfur-modified CR is a very dark and dirty blue. The NBR/PVC is very clean and bright. Mercaptan-modified polychloroprene ("W"-type) is not so severe a discoloring polymer as is sulfur-modified CR, but it is still a problem in light colors. We get occasional calls from customers complaining that the blue pigment in their compound is turning "green" upon cure. In many cases, the base rubber is CR and it is the yellowing of the polymer that is tinting the blue toward green. It may be wiser to make light colors from an NBR/PVC base to avoid these problems.

Display 1

NBR/PVC *Sulfur modified polychloroprene*

filler choice

The choice of filler will make a big difference in the way a compound will be colored. Air-floated kaolin clay (better known as "hard clay") is an outstanding cost / performance filler. Reasonably good reinforcement can be obtained at a very good cost. The problem with hard clay is that clean, bright colors will be hard to produce. The photos in *Display 2* show the same natural rubber compound filled with 50 phr each of hard clay, a high brightness water-washed clay (Polyfil HG-90), and a white silicate (Zeolex 80).
Then 3.20 phr of Akrosperse 802 Yellow EPMB were added to each. The quality of the resulting color is shown. The hard clay batch is a dirty, washed-out yellow. The brighter clay gives a cleaner yellow but is still somewhat washed out and the red undertone is lacking. Finally the white, semi-translucent silicate results in a very strong, bright, red-shade yellow.

To see what effect the filler has on cost of colorant, a color match was then done matching the two clay-loaded formulas to the silicate color. To get the same bright color of the silicate-filled formula, the table below shows the color and cost required to match:

Filler/colorant

Filler	phr	PHR Yellow MB	PHR TiO_2	Total Cost
Silicate	50	3.20	0.00	$53.21
Water-washed Clay	50	6.10	1.00	$62.84
Kaolin Hard Clay	50	12.90	5.00	$112.66

Further benefit of the silicate filler is improved processing like less mill sticking and smoother extrusion as well as better physicals. Although simplified, this is a good example how proper filler choice can save money.

Display 2

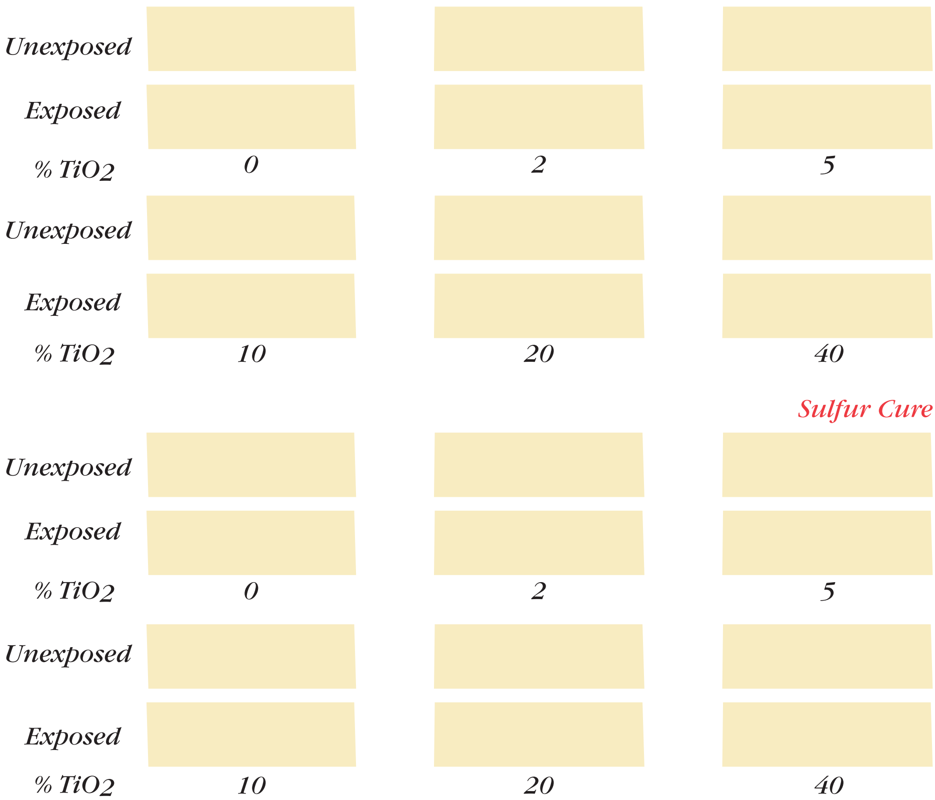
Silicate *Water-washed Clay* *Air-Floated Koalin Clay*

cure system

In most cases the cure system will depend on the rubber application requirements. It usually makes more sense to allow the compounder to choose the optimum cure system and then color around that. The primary choice is between peroxide and sulfur cures. Peroxide will result in the best initial color with the least subsequent color change after cure and outdoor aging. Sulfur cures will darken and yellow upon cure and after aging.

To explore the difference, a non-black EPDM-based compound was cured with peroxide and also with sulfur. Then progressively more TiO_2 was added to each compound. After one week of intense UV exposure, the change in color from an unexposed sample is easily seen in *Display 3*.

Display 3



Looking at the samples in Display 3, the first observation is the initial discoloration as well as the subsequent further discoloration in the sulfur-cured samples. As TiO_2 is added, the change in color is lessened upon UV exposure. The peroxide cure with just 2% TiO_2 had about the same color stability as 40% TiO_2 did in a sulfur cure. In addition, with just 2% TiO_2 the peroxide unexposed white color is as white as the 40% sulfur cure unexposed (there are tint differences). So if the cure system is optional, peroxide will often cost much less to color and will discolor less when aged.

If, however, a sulfur cure is preferred, the first thought should be to the rubber's specification. While certain sulfur accelerators are less discoloring than others, trying to avoid the slightly more discoloring accelerators at the expense of the compound's performance is usually not worth it. Do avoid the obviously highly discoloring accelerators like copper, lead or nickel dithiocarbamate. Also make sure accelerators are kept below levels that might bloom. A nice color can be ruined by parts that bloom.

miscellaneous materials

Process oils and plasticizers should, of course, be clean ones. Essentially this means not using aromatic oils. Most highly refined naphthenic and paraffinic oils are acceptable and virtually all monomeric esters (DOP, DBEEA, etc) have good color. Resins should be of the aliphatic type although some aromatic resins have very good initial color. Avoid any aromatic materials in outdoor applications.

Vulcanized vegetable oils come in various "colors". The brown Akrofax's should only be used in very dark colors. Light brown Akrofax's can be used in most colors except for pastels or whites (or where a highly consistent color is needed). White sulfur monochloride-cured Akrofax is used for the very light colors. The sulfurless Akrofax 758 White should be used in peroxide-cured, light colors.

Antioxidants and antiozonants of the amine type should be avoided. Phenolic antioxidants are the least discoloring and, if combined with a synergistic antioxidant like Akrochem Antioxidant 58, can provide good heat aging. Akrochem Antiozonant 70-TBPA in combination with 2-4 phr of wax can provide moderate-to-excellent non-discoloring ozone protection (depending on the polymer system).

Lead materials should be avoided in colored articles. Huber's Hysafe 510 is a good lead replacement for color compounds.

TROUBLESHOOTING COLORS:

FOLLOWING ARE A FEW PROBLEMS THAT WE HEAR ABOUT IN REGARDS TO COLORING RUBBER COMPOUNDS ALONG WITH POSSIBLE SOLUTIONS:

color changes upon mixing

A typical complaint is that white compounds are grayish or yellows are greenish. While obvious to most compounders, we do get inquiries asking why the color is shifting? It is almost always the result of contamination, typically from carbon black. This is one of the problems of mixing colors in the same mixer (or even the same building) with loose carbon black. Good, thorough cleanup is exceedingly difficult, if not impossible. The best solution is to isolate your color mixing from your black mixing. A second possibility is to have your colors or your black compounds mixed outside. Of course, once they are brought in, colored compounds should not be processed anywhere near black mixing equipment Finally, if colors must be mixed where black compounds are also mixed, be advised not to quote on light or highly consistent colors.

color changes upon curing

Sometimes the cured color is dramatically different from the uncured color. It's not always easy to determine the reason but here are a few things may cause a color shift upon cure.

Neutral base darkens on cure.

This is easily the largest problem with color control.

- The problem can stem from the polymer (see discussion of polychloroprene earlier), the filler, the cure system, the vulcanized vegetable oil, or the presence of lead products. Low loadings of color can not hide this color change. Changes can be made to the base compound or you can hide the color change with TiO_2 and additional color.

- A second cause of a base compound darkening may be temperature of cure. The curing temperature is an important factor in the neutral's final color. You may have done the color matching in the lab at 320F but the factory is running injection cures at 390F. It is a good practice to cure your uncolored neutral at the proposed factory curing temperature to see how stable the base compound will be. Again, titanium dioxide is the compounder's best tool in this case. Its ability to hide color shifts caused by curing temperatures is unsurpassed.
- Post-cured parts will often go through tremendous color changes due to temperature, particularly fluoroelastomers. In these cases, the pigment must be stable for the long post cure temperatures (300 - 500F), but also the neutral base compound's color shift must also be stabilized (again, usually with TiO_2).
- Most color pigments used today can withstand standard curing temperatures (300-380F). Even some colorants that in theory should not be used at the higher temperatures are successfully used due to the extremely short exposures to these temperatures. A true pigment burnout from excess temperatures is a rarity. Let Akrochem technical service advise you if you have temperature questions.

color "disappears" or is very weak

Certain color pigments (commonly called pyrazolones) can react with peroxides and cause the partial or total loss of color. If a peroxide will be used, it's best not to start any colormatching with pyrazolones (in the red and orange color range).

If the part is cured in a steam vulcanizer, certain pigments (primarily red salt products) are susceptible to extraction by steam or hot water. There are red pigments that will hold up in such applications but there may be issues with shade and sometimes cost. Talk to an Akrochem technical service provider for assistance.

bleeding colors

Occasionally some molded products will show evidence of color migrating to the surface of a part (often the mold cavity is discolored). Because pigments are not soluble in the polymer matrix (a chemical must first be soluble in order to migrate in a polymer. Only when it is at concentrations above its solubility does it then bloom) it is doubtful that the colorant is actually migrating. The probable cause is a plasticizer (e.g., ESO), process aid or an activator (glycols or stearates) that is coming to the surface during the cure. Sometimes a change in pigment type will help, but the wiser step is to reduce the loading or change outright the material that is actually bleeding. Many times the incompatibility exists only at molding temperatures and there may be no obvious sign of the material on the part after demolding. This "carrier" brings the pigment along with it either because the pigment is marginally soluble in the bleeding material or through physical means.

poor color from fluorescent pigments

Getting bright, glowing colors from fluorescents can be challenging in rubber. The optimized rubber formula for fluorescent colors is a peroxide-cured, transparent (or at least translucent) compound. Sulfur cures dirty the fluorescent colors; opaque compounds weaken the color (fluorescents are weak colors and thus provide the most color value when light can pass through the polymer). TiO_2 should be used only at very low levels (0.5 phr), if at all. If the ideal material can't be compounded, at least use clean translucent fillers (silicas or magnesium carbonate) to improve the color of the fluorescent. Then expect to use a lot of the fluorescent color to achieve any strength of color. Even though sulfur cures will cause a less-desirable color, the resulting "dirty" fluorescent color still can't be matched by organic colors. Also note that fluorescents are much more heat and light sensitive than most organic colorants.

differences in cure after color is added

Straight pigments rarely cause any cure difficulties. The same can be said for rubber bound ("masterbatch") colorants. Occasional problems may occur when large amounts (say 10 phr or more) of color masterbatch are used. The rubber binding the color may act as a diluent and cause a reduction in the state-of-cure (rheometer maximum). Various ways to improve this problem are: reduce color level (high color levels are usually due to high TiO_2 levels which can be reduced by cleaner fillers); incrementally add more cure to compensate for the diluent; reduce base polymer content in relation to the amount of polymer to be added by the colors.

An often overlooked problem is the use of SBR-bound color MB's in EPDM formulas. Most EPDM's cure significantly slower than SBR. SBR added to an EPDM preferentially cures first causing a scorchier material as well as an undercured EPDM portion. This is not a problem if the EPDM is a high diene type ($\geq$ 8% diene) or if the total SBR content amounts to no more than about 1 phr. The simplest solution is to use EPR bound colorants in EPDM stocks. Akrochem makes most color MB's in both EPR and SBR binders for optimum compatibility (other binders are available upon request).

dispersion of colorant after color is added

Dispersion of the colorant may vary from a minor issue to absolutely critical. Variables to consider include:

- type of pigment (most inorganic pigments disperse well; organics can be very difficult to disperse as well as messy)
- type of compound (the lower the shear during mixing - usually very soft compounds - the harder to get good dispersion). It is a rule of thumb to always add colors early in the mix when shear is high. In the case of upside down mixing or adding color to an already compounded neutral, easier-to-disperse color concentrates may have to be used.
- end product requirements (thin-walled extrusions, roll compounds, and printer's blankets all require maximum dispersion of colorant - as well as all other ingredients). Specially designed dispersions may be required like low viscosity, screened color masterbatches or the use of paste colorants.

In this issue we have touched on only a small portion of the coloring of rubber compounds. There is a world of additional information regarding the available colorants to the rubber industry. But because there are so many details involved in the proper selection of a color, we highly recommend using Akrochem's expertise to make this selection a little easier.

appendix

Formulations for Display 1:	CR-phr	NBR/PVC phr
Baypren 611 - KA8786	100.00	---
Krynac NV 870	---	100.00
Hubersil 162 silica	50.00	50.00
Elastomag 170 MgO	4.00	---
DIDP plasticizer	10.00	10.00
PEG 3350	2.00	2.00
Stearic Acid	1.50	1.50
Zinc Oxide	5.00	5.00
Akrosperse 626C Blue MB	1.00	1.00
Akroform ETU-22 PM	0.10	---
MC-98 Sulfur	---	1.50
MBTS	---	1.50
TMTM	---	0.20

Formulations for Display 2:	silicate	water-washed clay	air-floated hard clay
Natsyn 2200	100.00	100.00	100.00
Zeolex 80	50.00	---	---
Polyfil HG-90	---	50.00	---
HC-75 Hard Clay	---	---	50.00
ZnO	5.00	5.00	5.00
Stearic Acid	2.00	2.00	2.00
Sulfur	2.00	2.00	2.00
MBT	1.50	1.50	1.50
TMTD	0.20	0.20	0.20
Akrosperse 802 Yellow EPMB	3.20	3.20	3.20

Formulations for Display 3:	Sulfur	Peroxide
Buna EPT 2450	100.00	100.00
Hubersil 1613	25.00	25.00
Hubercarb Q-325 $CaCO_3$	25.00	25.00
Sunpar 150 Oil	10.00	10.00
ZnO	3.00	3.00
Stearic	1.00	---
Sulfur	1.50	---
MBTS	1.50	---
TMTD	0.60	---
BZX	1.00	---
Perkadox 14-40K-pd	---	6.00
TiO_2 as noted		