



use of waxes for ozone protection in rubber

Bloom. In many rubber products, the presence of bloom (the migration of a chemical to the surface of a rubber part) is a problem. However, there are times when the ability of a material to come to the rubber's surface can improve the product performance. One type of useful bloom will be discussed in this issue of Solutions: the use of waxes to provide ozone resistance (a well known but somewhat misunderstood process). A future Solutions will discuss the use of surface lubricants to provide a low coefficient of friction on the rubber surface (this "slippery" surface results in easier part installation or assembly, increased abrasion resistance, and reduced sticking of parts to other surfaces).

Ozone vs. Ultraviolet Surface Cracking

Waxes (both natural and petroleum derived) have long been used as process aids in rubber. They provide economical internal lubrication, mill and mold release, and improved compound flow. It was probably a fortuitous insight that connected compounds containing petroleum wax with less surface cracking of rubber parts exposed to an outdoor environment. It was believed that the cracking was caused by sunlight exposure, so the name "antisunchecking" wax was used. This is a misnomer. While the sun (via ultraviolet degradation) can cause crazing or "alligator skin" in rubber, wax provides little or no resistance to sunlight (or UV) deterioration. Petroleum waxes do provide protection against ozone attack of rubber parts. It's important to know the difference between ozone and UV degradation if parts come back from the field with surface cracking.

Ultraviolet energy will first crosslink the surface of double bond-containing rubber. This initially results in a hard, glazed rubber surface. Non-black articles are much more prone to this attack since carbon black is an excellent UV absorber. As the rubber surface gets more crosslinked it becomes embrittled and begins to craze or crack in various directions. This appearance leads to the term alligator skin. Eventually the rubber deteriorates away leaving behind only the non-black filler which is often mistaken for a bloomed chemical. UV inhibitors have minimal effect since most rubber is opaque (light does not pass through). Thus in most rubber, the UV reaction occurs only at the rubber surface while the UV inhibitors are buried in the compound. Higher than normal loadings (15 phr or more) of ZnO and/or TiO₂ will help UV resistance in colors. Antiozonants and waxes have little or no effect on this phenomena.

On the other hand, ozone (O₃) attacks a rubber's double bonds at the higher stress points. Thus black compounds are more susceptible to ozone, primarily due to the higher modulus of the cured rubber compared to non-black compounds. Ozone

cracks run in a rather orderly pattern perpendicular to the direction of the stress. Under static conditions, wax will create a film barrier to the ozone, preventing it from interacting with the rubber surface (sunlight, however, passes easily through the wax film and thus the UV interacts with the rubber surface). Akrochem has designed petroleum waxes to maximize these antiozonant properties under various environmental conditions.

Waxes as Antiozonants

Most rubber chemists are well aware that ozone resistance is improved by waxes. What is often not well understood is the mechanism of this resistance and how proper wax selection can improve part performance.

types of waxes

Paraffin Wax

Paraffins are linear carbon chains that are regular enough that they can be packed together tight enough to form crystals. The number of carbons in a chain (Carbon Number or C#) will range from 18 to 50 carbons (commercial paraffins are mostly in the 22 to 38 range). A critical concept here: *The higher the C#, the higher the molecular weight (MW), the higher the melt point*, and finally, the higher the optimum ambient temperature needs to be for the wax to bloom.* Also, paraffin waxes have a low affinity for petroleum oil which is another reason for their strong tendency to migrate out of a rubber compound.

Microcrystalline Wax

Microcrystallines are higher molecular weight than paraffins with C# between 30 and 80 with the majority between 45 and 55. Microcrystalline waxes also differ from paraffins in that the microcrystallines are extremely branched. This means they are amorphous (won't crystallize) and their complex structure resists migration. Their high affinity for oils is another reason microcrystalline waxes migrate very slowly from rubber compounds.

Formulated or Blended Waxes

These are blends of paraffin and microcrystalline wax. Usually the paraffin wax predominates with microcrystalline present at 30% or less. Often these blended waxes are incorrectly termed, "microcrystalline waxes" when they are actually mostly paraffin wax. These waxes are formulated to achieve specific results by modifying the blooming characteristics of the wax.

* For the purpose of this article "melt point" will be used as a reference point to discuss the approximate molecular weight of a wax. Melt point is a misnomer in the case of microcrystalline waxes. Their broad molecular weight distribution results in no clear-cut melt point (unlike paraffin waxes that have a relatively sharp melt point). Drop point (temperature at which a molten drop of wax falls from a thermometer tip) and congealing point (temperature at which a molten wax solidifies on the end of a thermometer) are used to more accurately classify microcrystalline waxes as well as blended waxes.

migration or blooming of waxes

The movement of wax to the surface of a rubber part depends on several variables:

- Molecular Weight or Carbon Number of the wax. The higher the C#, the higher must be the ambient temperature to input enough energy into the wax to provide sufficient mobility for it to migrate.
- Complexity of the wax. Branched waxes bloom slower.
- Concentration of the wax in the rubber. Once beyond the soluble threshold of the polymer, the more wax present, the greater the concentration gradient will “urge” the wax to come out.
- Ambient temperature. As the temperature goes up, the lower molecular weight waxes will be more soluble in the compound. Low molecular weight waxes already present on the surface of the rubber will be re-absorbed into the compound. Meanwhile, higher MW waxes will begin to migrate as the temperature increases.
- Polymer type as well as compound ingredients can effect wax bloom rate and amount. A non-polar additive like polyethylene can solubilize wax and reduce bloom. Although minor in effect, higher crosslinking will increase wax bloom. Higher filler loadings will slow bloom.

Almost all the wax film that blooms will be paraffin type. Microcrystalline is too bulky to bloom sufficiently to create an ozone barrier. However, its presence is important as we'll see in the designing of wax blends.

design of blended waxes

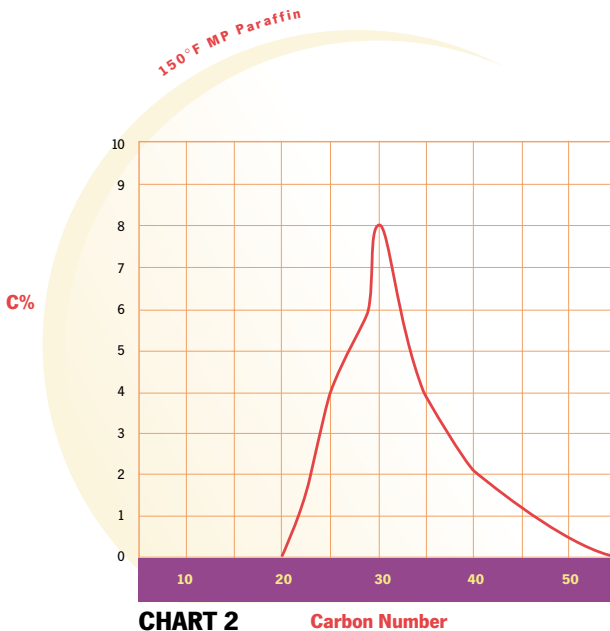
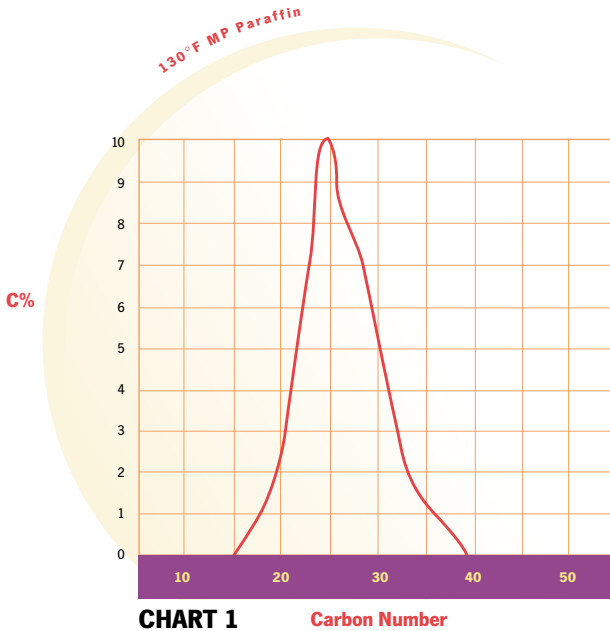
The basic reasoning behind blended waxes can be stated as follows: Ozone attacks rubber between the temperatures of 25°F (-4°C) and 130°F (54°C). To protect the rubber, there must be a wax film present on the surface of the rubber regardless of the ambient temperature. Depending on molecular weight and structure, each wax has an optimum temperature at which it will migrate to the rubber surface (see Table below).

Temperature (°F)	Temperature (°C)	Predominant Wax Carbon Number on Rubber Surface
32	0	23/24
50	10	25/26
68	20	27/28
86	30	29/30
104	40	32/33
122	50	37/38
131	55	41/42

The ideal wax would be one that creates a wax film barrier at all temperatures that ozone is active. No single wax can do this. Since paraffins will carry the burden of the ozone barrier, a blend of several paraffins of different melt points (molecular weights) is present in a good blended wax. Each wax will supply a certain percentage of carbon number wax such that a film is formed regardless of the ambient temperature. If you look at the carbon numbers of the 130°F paraffin wax (see Chart 1), most are around 24-26 carbons but there are carbons present from a low of 20 to a high of about 34 (there are a few of carbon number higher than 34, but probably not enough to make much difference in the bloomed film). The 150°F paraffin

DESIGN OF BLENDED WAXES: c o n t i n u e d

wax (see Chart 2) centers around 31 carbons with a range of about 25 to 42 carbons. Finally, a typical microcrystalline wax (see Chart 3) is a broad molecular weight distribution centered around 42-43 carbons. When these waxes are blended the carbon number charts are “overlapped” (Chart 4) such that there will be wax of the appropriate carbon number available to bloom regardless of the ambient temperature. The paraffin waxes of varying melt points provide most of the ozone-resisting film. However, the microcrystalline wax plays another important role in a blended wax.



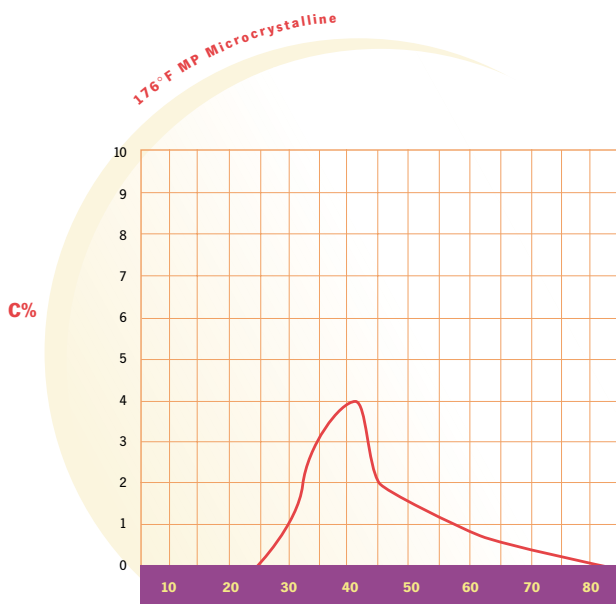


CHART 3 Carbon Number

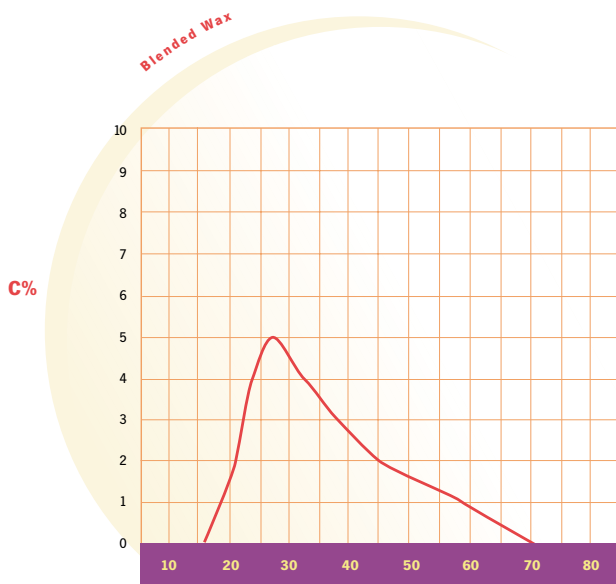


CHART 4 Carbon Number

When paraffin wax comes to the surface of a rubber part, it forms a highly crystalline, inflexible, poorly-adhering film. The pure paraffin forms an oversized crystalline structure that permits “holes” to be present in the barrier such that the wax is actually permeable to gas (air). Thus ozone can still reach the rubber surface. By disrupting the macrocrystalline structure of the paraffin wax with as little as 4% branched wax (microcrystalline), a more amorphous, very fine crystalline barrier is created that is now impermeable to ozone. In addition to the improved ozone resistance, the disruption of the paraffin crystallinity by the microcrystalline wax also makes the wax film more flexible. A pure paraffin film is very brittle and tends to crack easily with minimal flexing. Microcrystalline wax reduces the crystallinity and allows the wax film to move with the rubber part. Instead of flaking off at the first movement of the rubber the wax “bends” and as a result lasts longer. The microcrystalline wax also adheres to the rubber surface better than the paraffin wax, again aiding a longer lasting wax film.

Thus the optimum wax for most field applications is a blend of several molecular weight paraffin waxes with a small amount of microcrystalline wax. Akrowax™ 5026, 5030, 5031, and 5084 are in this class of blended wax. Of course, the nature of these blends lends itself to designing the wax to meet specific needs. Let’s look at one of the special needs of rubber compounders: ozone chamber testing.

Ozone Chamber Testing

ASTM D 1149 and D 1171 ozone chamber testing are typically done at 40°C (104°F). Whether this is an appropriate test temperature is debatable, but the important thing is to optimize your wax for this test. As the carbon number table shows, at 104°F the carbon number most present on the rubber surface is around 32. And from the paraffin wax discussion, you can see that the 150°F wax distribution is centered near this carbon number. Thus for ozone chamber tests, the wax blend should be primarily composed of 150°F paraffin wax. Some microcrystalline is still needed for optimized wax performance. This type of “ozone chamber wax” is found in Akrowax 5026.

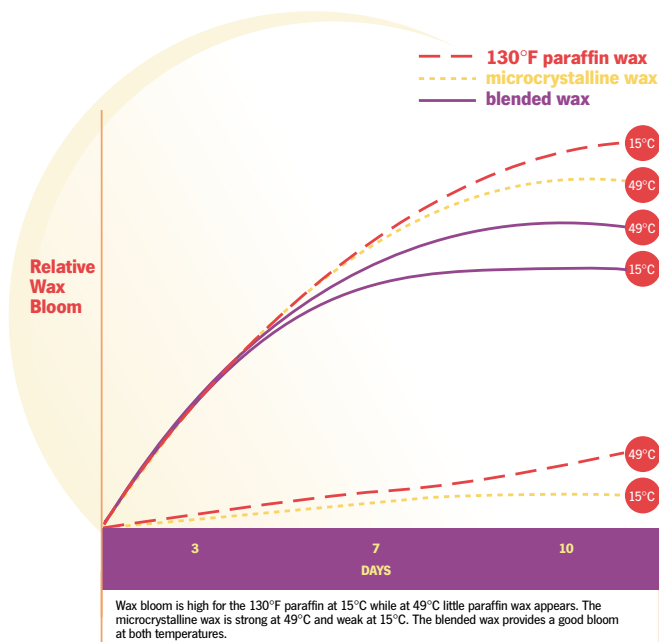
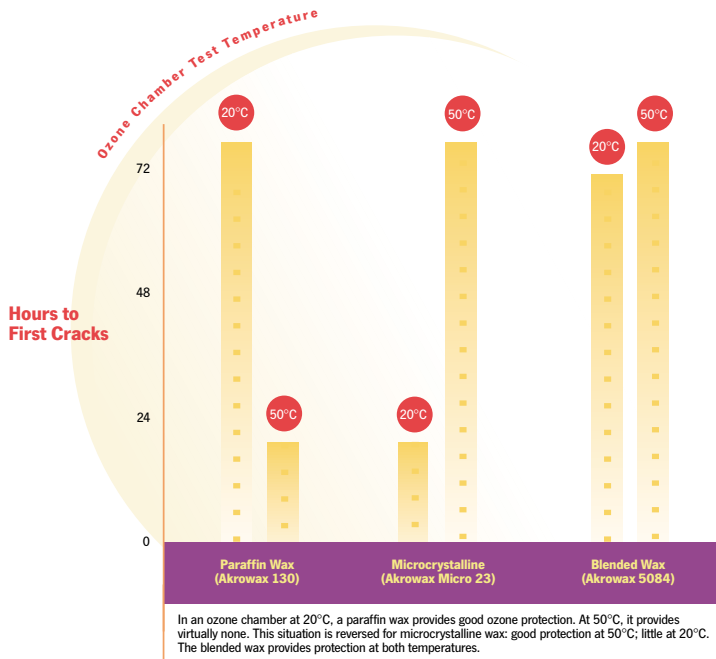
A study was done to look at paraffin wax melt point and ozone chamber test temperature correlations. A natural rubber compound had 5 phr of either a 130°F melt point paraffin or a 150°F melt paraffin. Samples were conditioned for 24 hrs at 40°C. (note that preconditioning should be done at the same temperature at which the ozone samples will be exposed). Testing was done at 50PPHM ozone concentration, 25% strain, for 72 hrs (bent loop method) at 40°C. Results are as follows:

5 phr 130°F MP Wax	Moderate cracking
5 phr 150°F MP Wax	No cracking

In a further study, at 10 phr wax, there is just enough of the higher carbon number wax in the 130°F paraffin to provide a film that will pass this ozone test without cracks. By comparison, the 150°F paraffin at 10 phr will pass this ozone test even at 60% strain.

The graphs on the following page further emphasize the importance of blended waxes for all-weather ozone protection:

DESIGN OF BLENDED WAXES: c o n t i n u e d



Following is a brief summation of the Akrochem blended waxes and how they may be used in specific environmental situations.

Akrowax 5026	Designed for ozone chamber exposure at 40°C
Akrowax 5030	Designed for exposures primarily $\geq 40^\circ\text{C}$
Akrowax 5031	Designed for exposures primarily $\leq 40^\circ\text{C}$
Akrowax 5084	Akrochem's most balanced blended wax.
Akrowax 5050	A bimodal wax for low and high temperatures

summary of blended waxes

Special combinations of wax may be required in particular situations. For example, a part that will be used in a colder climate (Canada or even Siberia are examples) may require additional low temp paraffin above that provided by a blended wax. In this case a 130°F melt paraffin would be combined with a lower temperature blended wax for better ozone protection. Also, remember that when a blended wax is used, typically it should be used at a higher concentration than a narrow molecular weight distribution wax (like a single paraffin wax) to insure that sufficient wax comes out at all needed temperatures. In other words, 3 phr of a 130°F paraffin may be sufficient to provide a wax bloom at 20°C (68°F) but it will provide minimal bloom at 40°C. For a blended wax to provide as much bloom at 20°C and still provide good bloom at 40°C, 5 phr of blended wax may be needed.

Dynamic, Intermittent and Static Exposure

Some consideration should be made for the functionality of a rubber part and the amount of wax to be added. Wax protects rubber from ozone under static conditions. A rubber part that is essentially static in service can be well protected by wax alone. But as a part becomes more dynamic, wax may become a detriment to ozone protection. The theory behind this rather odd fact is that as the dynamic movement of a part occurs, the wax film breaks and exposes narrow pieces of rubber to ozone attack. This concentrates the effect of ozone where the wax has broken and causes earlier failure.

Therefore, as a part becomes more dynamic there becomes a greater need for chemical antiozonants to function synergistically with a wax. Chemical antiozonants (primarily PPD's or p-phenylenediamines) are typically combined with waxes to provide optimum ozone protection under both static and dynamic conditions ("intermittent" service). A future "Solutions" will cover chemical antiozonants in depth but for now it is enough to say that wax and chemical antiozonants should be used together to maximize ozone resistance. The proper loading of each will depend upon the part's dynamics, the expected ozone environment, and how long the part is expected to last. Below is a rough rule-of-thumb for wax and chemical antiozonant loadings:

	Wax	Chemical Antiozonant
Static Application	3 to 10 phr	0 to 1 phr
Intermittent Application	1 to 3 phr	1 to 3 phr
Highly Dynamic Application	0 to 1 phr	3 to 5 phr

Note that a small amount of wax will often help ozone resistance of dynamic applications, primarily by bringing the chemical antiozonant to the surface. High amounts of wax (i.e., 5 phr), however, in a dynamic part will decrease flex fatigue resistance. For the same reason chemical antiozonants are used in dynamic parts for ozone resistance, the chemical antiozonants are essential to improved flex fatigue. Most rubber parts in reality are a combination of static and dynamic functioning and thus should have the intermittent loadings of wax and chemical antiozonants for best ozone and flexing performance.

conclusion

Petroleum waxes have many uses in rubber including internal lubrication and release from metal surfaces, but the most essential use is to improve ozone resistance. This occurs by the formation of a protective wax film as well as the wax bringing chemical antiozonants to the surface. The extent and temperature of wax bloom can be compounded into a formula by proper selection of the right waxes.



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