

BLOOMS AND BLOOM LIKE PHENOMENA

A H L R Nilmini

There is no doubt that every rubber technologist and analyst knows what is meant by the word bloom. However, investigations have shown that it is relatively rare to see a true chemical bloom and that most of the so-called blooms are due to other effects.

Generally, appearance of whitish and some times yellowish powdery deposits on many rubber compounds prior to, and also subsequent to curing, is called "blooming". However when the problem is carefully analyzed, several phenomena other than real blooming are involved here.

When does blooming occur

Blooming occurs when a given material has limited solubility in the rubber used, and when this solubility is temperature dependent. A material that is completely insoluble in a rubber will not bloom, neither a material which is highly soluble.

True blooms

A true bloom is a thin layer, on the surface of the rubber article, of one of the chemicals either added before, or produced during, vulcanization which results from migration of that chemicals from the bulk of the article to its surface.

A chemical, which blooms, must,

- Have a limited but appreciable solubility in the rubber
- Be present at concentration greater than this solubility at storage temperature.

This excess will exist as discrete particles through out the mass of the rubber either because it has dissolved or because, having dissolved at the temperature of vulcanization, or crystallized out on cooling.

Materials that can give true blooms

Sulfur

Free sulfur is probably the most common substance to give a true bloom and in a vulcanized product such as bloom is due to undercure. This blooming is more prominent in natural rubber compared to SBR or many other synthetic rubbers. Solubility of sulphur in rubber is temperature dependent, and for example, in natural rubber its solubility is about 6 to 8 pphr at 100°C while at 30°C only 1.8 to 2.5 pphr may be soluble.

Disadvantages of sulfur blooming

- Calendered material loses tackiness, which affects further processing and assembly of blanks. Ex: In tyre cord, conveyer belts laminated articles, this loss of tackiness can become a serious problem.
- When blanks with a coating of bloomed S are vulcanized, uneven cure can be seen.
- In light coloured products, dark spots appear when serious accumulation of S has taken place, and in the rest of the surface, there are brownish yellow patches.

Control of S blooming

- Reducing the sulfur level in the formulation of given compound which will require adjustments in the acceleration types and quantities used.
- Use of a different form of sulfur, which is known as soluble sulfur consists of 8-membered rings of sulfur atoms while insoluble sulfur is made up of long polymeric chains.

Insoluble sulfur is produced by rapid cooling of a sulfur melt and this product is usually marketed in the form of pastes. As the stability of insoluble sulfur is temperature dependent one has to be careful to control processing temperature if the purpose of using this expensive material is to be realized. At high temperatures, the insoluble sulfur reverts to the soluble form. Therefore, we should note that the use of insoluble sulfur prevents the blooming only in uncured stocks and blanks but not in vulcanisates.

Accelerators

Zinc dithiocarbamates are responsible for blooms and of the three common ones, the dimethyl, diethyl and dibutyl- dithiocarbamates, it is the middle one, which shows the most rapid and, over a period of time, the densest bloom. The order of solubility is ZDMC < ZDEC < ZDBC and it is therefore concluded that the soluble fraction of ZDMC is relatively low, resulting in a low rate of migration, whilst ZDBC is sufficiently soluble for the solubility limit not normally to be exceeded and thus for there to be no bloom. It is unfortunate that ZDBC gives a slower rate of cure than the methyl or ethyl homologues and that it is therefore not always practicable to use it.

Of the other commonly used accelerators, mercaptobenzothiazole and Zinc mercaptobenimidazole have also been observed to bloom.

In accelerator, blooming Tetramethyl thiuram disulphide is worse than the monosulphide derivative. While dimethyl diphenyl thiuram disulphide causes blooming. In fact blooming due to the presence of a thiuram type accelerator is caused by the corresponding Zinc dithiocarbamate. In acceleration with thiurams they are first converted to the dithiocarbamate and this is why the onset of cure with thiurams is slower than with dithiocarbamates.

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In accelerator blooming tetramethyl thiuram disulphide (TMTD) blooms more than the monosulphide derivative (TMTM) while Dimethyl diphenyl thiuram disulphide causes little blooming. In fact blooming due to the presence of a thiuram type accelerator is caused by the corresponding Zinc dithiocarbamate. In acceleration with thiurams they are first converted to the dithiocarbamate and this is why the onset of cure with thiurams is slower than with dithiocarbamates.

Non blooming accelerator systems for EPDM

In the case of EPDM vulcanisates, which usually require very large levels of accelerator blends to obtain an acceptable level of curing, blooming can be a common problem. This can be overcome by replacing the dithiocarbamates used with dithiophosphates. There are special accelerator preparations available for the curing of EPDM, but they have to be used in large concentrations, and are expensive. They seem to be blends of common accelerators.

Bloom like phenomena

What other effects that can produce a bloom-like surface to a rubber article. Three groups may be identified and these are,

- Modified blooms
- Pseudo blooms
- Surface contamination

It is also valid to include other effects, which on occasion have been confused with blooms. These are,

- Staining or discoloration
- Hazing

Modified blooms

Certain chemicals in a vulcanizate can react with constituents of the environment and this result in a significantly different mechanism of blooming to give a chemical at the surface which is different from that which migrates. A paraphenylene diamine (PPD) antiozonant, for instance, reacts with ozone at the "surface" of the rubber and thus, regardless of whether "surface" is measured in millionths, thousandths or fractions of a millimeter, a solute concentration gradient is again set up and migration occurs with the PPD oxidizing to produce a surface skin until that skin is sufficiently thick to prevent further ozone penetration.

Paraphenylenediamines may also bloom by the "true bloom" mechanism and it is therefore important that they should only be added at levels up to their solubility. Although this is usually the case when a formulation is originally devised, subsequent modifications without a full realization of their significance have been known to take formulations "over the limit".

Zinc stearate may also produce a modified bloom. With a solubility in rubber of some 0.3% zinc stearate should inevitably bloom as it is usually present in excess of 1% but its solubility is greatly increased by complexing with amines and, as these are generally present as cure residues, it normally remains in solution. However reaction with water vapor at the rubber surface will lead to the formation of insoluble basic zinc stearate, which has all the appearance of a true bloom but is chemically quite different from the oily zinc stearate.

All the chemicals which give modified blooms can also give true blooms if added or generated at concentration in excess of their solubility in the rubber. Normally these factors are appreciated in designing a formulation but subsequent modification or fine tuning to a particular specification has been known to cause problems.

Pseudo blooms

On a very large number of occasions, it has been found that the matt surface which has developed on an initially smooth and shiny surface has been due to surface degradation of the rubber itself. The pitted surface giving enough light scattering to suggest a bloom. On certain occasions, the rubber has been observed to degrade around a particle of filler, leaving a ball - in - a - cup effect, which has lead people to suggest that the fillers have bloomed. Because of the complete insolubility of fillers in rubber, and the mechanism of blooming described earlier it will be appreciated that this is impossible.

Surface contamination

It is always difficult to decide by visual inspection whether a surface deposit is a bloom or contamination and it then rests with the analyst to identify the surface materials to such an extent that this can be resolved. One of the most obvious causes of surface contamination is silicone oil, used as a mould release agent. Not only does it impart an oily film to the surface but it also gives a base to which dirt and dusting powders may adhere.

The washing of rubber products also gives rise to contamination if rinsing is inadequate and both inorganic salts and organic materials have found their way on to the surface of rubber articles by this route. Inorganic fillers, used as dusting agents, tend to be present in the air of most factories and can adhere to freshly moulded rubber surfaces, giving the appearance of a bloom.

Hazing (of transparent rubbers)

Haze is defined as a cloudy appearance within or on the surface of a transparent article and from a visual inspection It is often difficult to distinguish between haze and a bloom. Blooms and surface breakdown have already been discussed so we must now consider opacity within the bulk of the rubber itself. This will result from the presence of insoluble particles, micells or droplets (in the case of liquids) having a different refractive index from rubber and so able to cause light

scattering. One of the commonest causes of this is the use of Zinc oxide either of the wrong grade or in excessive amounts, so the problem can be eliminated by the use of special fine-particle grades at levels not exceeding 1 pphr.

On the other hand, calcium oxide can cause this effect even at the low levels required for desiccant purposes whilst the maldispersion of otherwise suitable compounding ingredients is a further threat to transparency.

Staining and discolouration

Although these terms appear very similar, their use differentiates between the staining of a materials in contact with the rubber and the discolouration of the rubber itself. The majority of the former (staining) are due to reactions between different chemicals in the two materials. Dithiocarbomates or free sulphur in the rubber may react with copper or iron in the dyes of adjacent materials to give dark coloured stains whilst an excess of copper from a dye, lead from impure zinc oxide, manganese or iron from whitening or titanium dioxide can also discolour an unfilled or white rubber product.

The effects of using staining antioxidants are well known and these can result in purple, blue or brown discolourations in a light coloured product whilst certain phenolic antioxidants can give a pale pink colour to clear or lightly coloured products. A pink colour may also be observed when zinc diethyldithiocarbamate is used in the manufacture of latex products. This is light-induced phenomenon known as 'PINKING' which can be removed by a wash in dilute potassium hydroxide solution.

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