Ram Charan
PRODUCT DEVELOPMENT INFORMATION
VOLUME 3
ISSUE 8
NOVEMBER 2013

BLOOMING IN RUBBER

An Overview With Analytical Path

A discolouration or change in the appearance of the surface of the Rubber due to the migration of solid or liquid materials/substances, is termed as blooms in Rubber

Blooms can be divided into

a. True blooms
b. Modified blooms
c. Pseudo blooms
d. Surface contamination

Mechanism of Blooming:

The substance of crystalline in nature, which blooms must have a limited but appreciable solubility in Rubber and be present in excess of this solubility. This excess will exist as discrete particles throughout the mass of the rubber either because it has never dissolved or because, having dissolved at the temperature of vulcanization, it has crystallized out on cooling.

In thus, crystallizing it must be assumed that local strain is set up in the rubber displaced by the formation of the crystal. This strain results in pressure on the crystal, the solubility of which is increased thereby. At the free surface crystals of the material can form without distortion of the rubber and the solubility will be unaffected.

The free energy of crystallization will therefore be less at the surface than in the bulk of the rubber; the solubility of the substance will also be slightly less. There will therefore be a concentration gradient of dissolved material which will cause diffusion from the inside towards the surface and this will persist unitl all the material crystallized in the bulk has dissolved under the influence of pressure and diffused outwards.

The magnitude of the increased solubility due to pressure will of course, be minute, as also will the concentration gradient within the rubber but large forces are not necessary to account for the observed phenomena.

True Bloom:

The substance which has limited but appreciable solubility in the rubber matrix and be present in excess of its solubility, comes to the surface of the cured rubber through crystallized out on cooling is referred to as True Blooming.

Example is wax blooming, Free Sulphur blooming (also from undercure in the vulcanized product).

Others: In Zinc Dithio carbamate family the rate of solubility is in the order of ZDMC<ZDEC<ZDBC. But the diethyl group gives the densest bloom, whilst ZDBC is sufficiently soluble for the solubility limit & thus for, there is no bloom.

Similarly MBT, ZMBT also gives true bloom.

Modified Blooms:

The Chemical substance present within the matrix of a rubber Vulcanisate react either deliberately or not, with the constituents of the environment results in modified blooms.

Eg. 1. Paraphenylene diamine (PPD) anitozonants when used in excess.

2. Zinc Stearate when used in excess → initially it forms the oily bloom but in moist atmosphere forms basic solid zinc stearate film which is completely insoluble in rubber results in modified bloom. (A true zinc stearate bloom dissolved back into the rubber by heating.

Pseudo Blooms:

The degradation of the rubber surface around some type of fillers gives the illusion of pseudo bloom.

Eg. When Calcium / Zinc Carbonate used in the rubber formulation gives the impression of pseudo bloom as the degradation of rubber surround the filler particle resulting in the exposure of these particle in a crater of rubber, as the inorganic materials cannot migrate to give blooms.

Surface Contamination:

An undesired surface deposit on the rubber part is termed as surface contamination.

It can happen either from

a. Silicone oil which gives the greasy bloom and serve as a base for other dusty materials stick on the surface.

b. Inorganic & organics contained in washing & rinsing solutions.

c. Filler dust in factory atmosphere.

HAZING:

It is defined as a cloudy appearance within or on the surface of a transparent article which results in the opacity of the product.

Hazing is caused from insoluble particles of micelles or droplets.

Eg. Zinc Oxide wrong grade or over dosage , Calcium Oxide or other poorly dispersed materials.

Staining/Discoloration:

Stain/Discoloration is described as the effect produced on the Rubber Product in contact with other substrates.

Main causes: Free Sulphur or Dithiocarbamate in contact with copper, Traces of iron or copper within the Rubber product, too high of Zinc Oxide in the presence of Lead.

Generally if the copper level > 20 ppm, Iron>150 ppm → results in Stains/Discoloration.

Pink colour – Phenolic antioxidant

Pinking in latex goods – due to ZDEC induced by light when more than the solubility limit is used and can be removed by dilute Potassium Hydroxide solution.

Purple, Blue or Brown stain – presence of PPD (paraphenylene diamines) staining antioxidant.

INFERENCE ON BLOOMING:

ANY SUBSTANCE WHICH IS PRESENT IN THE RUBBER MATRIX BEYOND THE SOLUBILITY LIMIT OF THE SAME WILL END UP IN BLOOMING.

BLOOM ANALYSIS:

Can be done by examination of the surface as it stands or to attempt to remove any bloom present and carry out a subsequent analysis on the separated bloom.

1) Analysis on the blooms on the surface without attempting to remove through

a) Spot test

b) Multiple internal Reflectance

c) Scanning Electron Microscopy.

a) Spot test is restricted to the detection of free sulphur.

i) Behaviour with Carbon Disulphide:

If one small drop of Carbon disulphide is spotted on to the bloom the drop spreads out and then dries off, leaving a clean dull circular area surrounded by a line of recrystallised sulphur. The

The yellow crystalline appearance of this ring seems quite characteristic and is not obtained with accelerators and antioxidants.

ii) Kirchhof's Piperidine Test:

The surface of a white or brightly coloured rubber is spotted with piperidine. In the presenc e of free sulphur a yellow or deep orange-red colouration occurs presumably due to the formation of polysulphide piperidine compounds.

b) Multiple Internal Reflectance:

c) Scanning Electron Microscope – through x-ray elemental analysis.

2) Removal of Bloom for analysis:

This can be done either by wet or Dry method

a) By Dry Method:

1. To detect Sulphur in a bloom on an article, fold in four a piece of filter paper(preferably the slow-absorbing, alkali-resistant type) and rub one of the fold edges over the surface; if the bloom is light, first treat the surface with a drop of carbon disulphide, and then rub the paper round the outline left when the solvent evaporates. Unfold the paper and add 1 drop (about 0.05 cm3) of strong (20 – 30%) sodium hydroxide solution, followed by 1 drop of pyridine. A blue-green colour in the pyridine, rapidly succeeded by an orange o r brown stain on the paper at the fold, indicates the presence of Sulphur.

2. Also the surface blooms can also be analysed using thin layer chromatography which will often identify the bloom components. And is also followed by the analysis by TLC, LC, IR, DSC or melting point apparatus,.

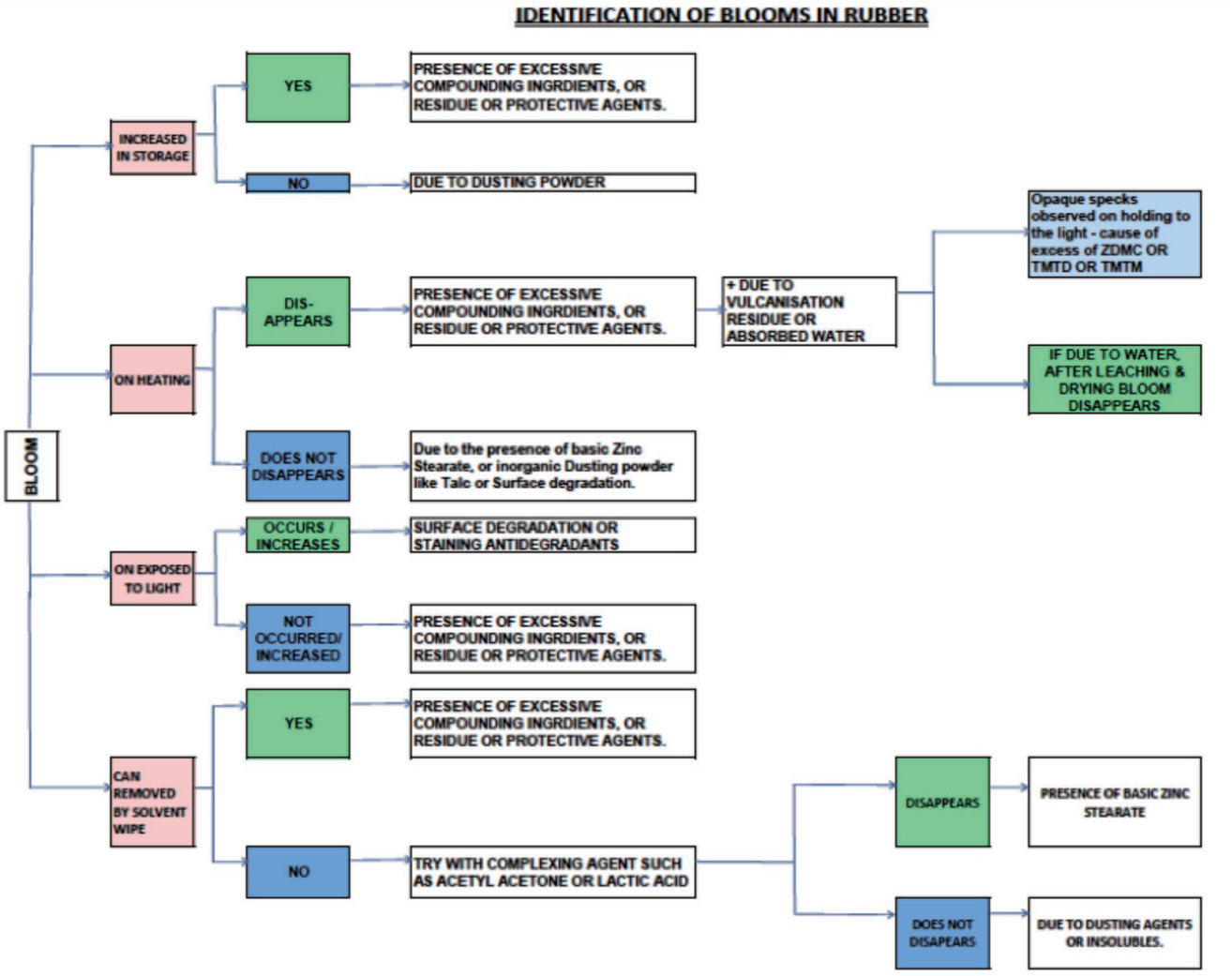
b) By Wet Method:

i. Through swaps moistened with chloroform or acetone or methanol or a mixture of acetyl acetone & 2-propanol and extracted the swabs to obtain solutions of the removed chemicals for thin layer chromatographic analysis.

Limitation of this method some of the chemicals beneath the surface might also get extracted & may give false anlaysis. This can be overcome by reducing the swap temp from +20 deg.C to -70 deg,C.

ii. The blend of acetyl acetone & 2-propanol is used for insoluble basic zinc stearate / palmitate bloom by soaking for up to 93 hrs. @ -26 deg.C and further analyasis by atomic absorption spectrometry and gas chromatography.

IDENTIFICATION OF BLOOMS:



Ram Charan Company | Samson Tower, 403, L – Pantheon Road, 6th Floor, Egmore, Chennai 600 008. Tamil Nadu, India.
Phone : +91 44 4353 9040 • Email : mktg@ramcharan.org • Website : www.ramcharan.org