

# ***Understanding BLOOM***

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***Prepared by KP Ho***  
***- Performance Additives***

# Introduction

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“Bloom” is caused by the migration of solid or liquid compounding materials which have a limited solubility in the polymer matrix.

Bloom includes dry bloom and wet bloom which is also known as “exudation”, “bleeding” or “oily bloom”.

Very common, bloom refers to the initial formation of star-shaped clusters when solid compounding materials re-crystallize at the vulcanisate surface. This is due to the fact that many of the rubber compounding materials have limited compatibility with the elastomer and separate out at the latest after vulcanizing and subsequent cooling to room temperature. Blooming is a diffusion controlled process.

Development of bloom can be stimulated mechanical or chemically. e.g. a chemical stimulation is the occurrence of whitish or grayish fingerprints on vulcanisate. This is caused by acetic acid contained in perspiration.

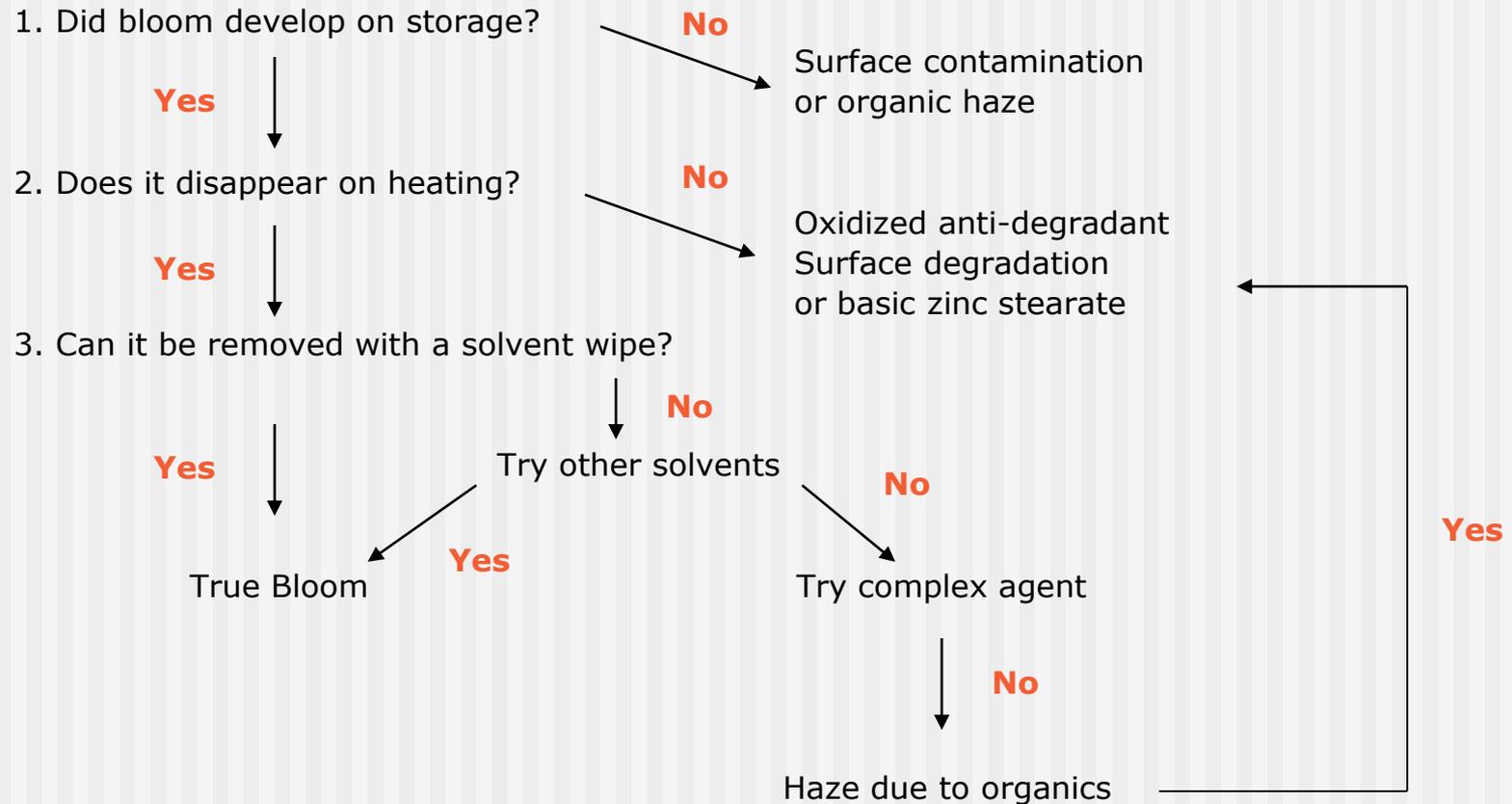
# Introduction

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## Bloom-like Phenomena

1. True blooms
2. Modified blooms – protective coats
3. Pseudo blooms – surface degradation of rubber itself
4. Surface contamination
5. Staining or discoloration
6. Hazing

# Simple Tests to identify bloom type



**Other instrumental analysis : Multiple Internal Reflectance infra-red spectroscopy (MIR)  
: Scanning Electron Microscopy (SEM)**

# Color changes and their significance in “Bloom” analysis

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**1. Is the color change light induced? (mask part of sample for reference)**

**Grey/Brown**

**- amine antioxidant**

**Pink**

**- phenolic antioxidant**

**2. Is the color change heat induced?**

**If yes with stickiness/embrittlement**

**- oxidative degradation**

**If yes without stickiness/embrittlement**

**- amine antioxidant**

**3. Is the color change patchy?**

**Reaction of external contamination with rubber chemicals**

**4. Does color change appear after laundering or contact with metal?**

**Copper/Iron reaction with dithiocarbamates**

**5. Does color change accompany poor ageing?**

**Further evidence for copper/iron contamination**

# Blooming of Crystalline Substances

- such as paraffin waxes or sulphur

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*Limited solubility in a given elastomer and a dosage level above the solubility limit are the main causes for a substance to develop bloom.*

Most chemicals are more soluble in hot rubber than cold rubber. Also, they are more soluble in unvulcanized rubber than vulcanized rubber.

A substance completely soluble in the rubber at mixing temperatures is mostly compatible with the elastomer in the uncured state. After vulcanizing and as soon as the vulcanizate cools the substance will begin to crystallize.

The crystal growth within the cross-section of the rubber is limited by strain development around the crystals. At the vulcanizate surface crystal growth will continue due to much less strain. The concentration gradient will cause the solute substance in the bulk to migrate to the surface and the crystal in the bulk to dissolve. Migration will end when all material above the solubility limit has formed crystals at the surface.

# Protective Waxes

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The wax layer acts as a physical barrier in order to protect vulcanizate against ozone attack.

## Paraffin Waxes

- Mainly consist on n-paraffin (n-alkenes) with small amount of branched paraffin (iso-alkenes).
- Generic formula  $C_nH_{2n+2}$  where  $n=18$  to  $50$ .

## Microcrystalline Waxes

- Mainly branched chain with some naphthenic content.
- H/Cs have approx. 34 to  $>70$  C-atoms. Therefore, higher average MW and higher Mpt. compared to paraffin wax.

In general wax dosage varies between 3 and 12phr.

For more dynamic applications, e.g. tires and conveyor belts the dosage can be as low as approx. 1.5phr. Additional protection through effective antiozonants is a must in these cases.

For cellular rubber wax may be used at up to 20phr.

# Sulphur Bloom – “A curse to the rubber industry”

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Usually happened when vulcanizates are under-cure.

Also, the level used is significantly above their solubility limit within the based polymer(s).

Particle size of sulphur is critical. A 10% retain on 200 mesh screen is essential. High coarseness gives uneven concentrations and spotty bloom leading to either stain or spots on vulcanizate.

Insoluble sulphur is recommended to prevent bloom. Taking note that processing temperature and storage conditions must be taken care.

# Types of Sulphur

Two basic types of sulphur – Soluble & Insoluble

Phase	Symbol	Form & Remark
Crystalline S-Rings ( <i>SOLUBLE in CS<sub>2</sub></i> )	S <sub>α</sub>	Rhombic modification M.pt. 113 deg C.
	S <sub>β</sub>	Mono-clinic modification M.pt. 119 deg C
	S <sub>χ</sub>	Mother-of-pearl like modification M.pt. 107 deg C
Amorphous S-chain ( <i>INSOLUBLE in CS<sub>2</sub></i> )	S <sub>λ</sub>	Sometimes could be micro-crystalline. Obtained as insoluble amorphous residue by extraction with CS <sub>2</sub> when quenching the melt after it has been heated at various temperatures.

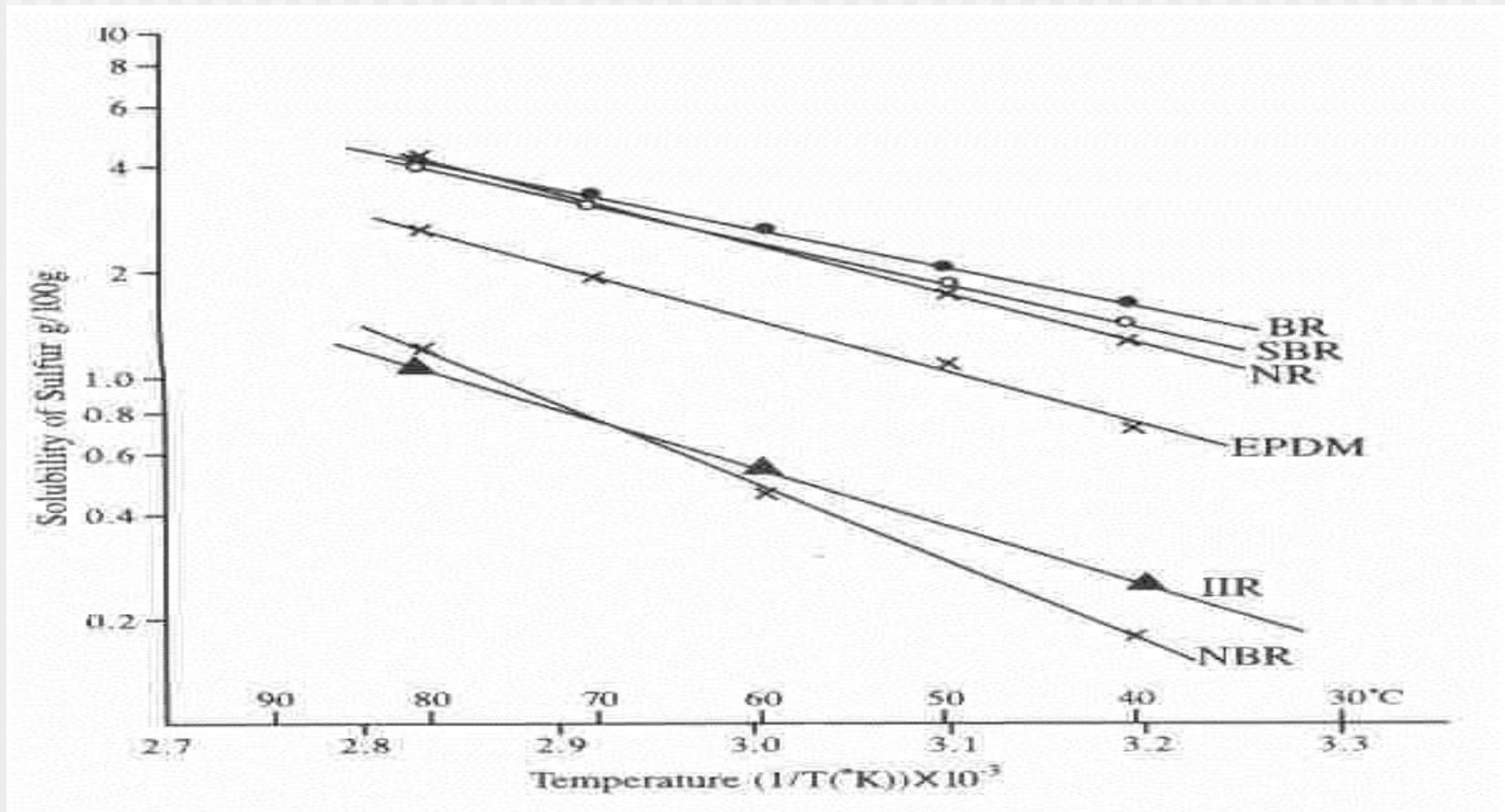
**When sulphur is insoluble in CS<sub>2</sub>, it is again insoluble in rubber polymers**

# Factors to be noted with Insoluble Sulphur

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- **Insoluble sulphur agglomerates due to electro-static charge, thus very difficult to disperse**
- **Insoluble sulphur reverts into soluble sulphur at above 80 deg C**
- **Blending and dispersion of insoluble sulphur must take place at temperature below the critical reversion point**
  - **Applies to any further processing, like extruding and calendering**
- **Inorganic and organic bases (oxides and hydroxides), oxygen containing solvents and cationic wetting agents can also increase tendency to revert**
- **Take note on accelerators system in which the activators are not too alkaline**
- **MBT (Accelerator M) should never be used with insoluble sulphur**
  - **Even NOT to store insoluble sulphur next to MBT**

# Sulphur Solubility in Standard Polymers



# Accelerators

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**TMTD(Tetramethyl thiuram disulphide)** is well known to cause bloom, particularly when used as sulphurless curing system. A whitish bloom is formed which consists of its reaction product ZDMC (This applied similarly for TMTM which gives higher yield of ZDMC).

Bloom can occur at only 0.5phr although it is occasionally used at 3phr without any blooming problems in some cases.

Replacing part of TMTD with TETD and/or DDTS(Dimehtyl diphenyl thiuramdisulphide) could avoid bloom. Simultaneously, use of mercapto or sulphenamide type accelerators can be helpful.

**TBTD** is totally soluble in most rubbers and so is the ZDBC reaction product formed. So it does not bloom.

# Accelerators (cont')

Solubility of Compounding Materials in Cyclohexane at RT (g/100g)  
(Cyclohexane is used as a model for NR)

<b>ZMBT</b>	<b>0.01</b>
<b>Zn Stearic</b>	<b>0.1</b>
<b>DOTG</b>	<b>0.3</b>
<b>MBT</b>	<b>0.3</b>
<b>MBTS</b>	<b>0.3</b>
<b>TMTD</b>	<b>0.3</b>
<b>TMTM</b>	<b>0.3</b>
<b>ZDMC</b>	<b>0.5</b>
<b>DPG</b>	<b>0.8</b>
<b>OTOS</b>	<b>0.8</b>
<b>Sulphur</b>	<b>2.0</b>
<b>TETD</b>	<b>4.0</b>
<b>Stearic Acid</b>	<b>5.0</b>
<b>DTDM</b>	<b>7.5</b>
<b>CBS</b>	<b>8.0</b>
<b>OBTS</b>	<b>14.0</b>
<b>ZDBC</b>	<b>16.0</b>

# Accelerators (cont')

## Solubility of Accelerators in EPDM

EPDM has low unsaturation and therefore required high levels of effective accelerators with sulphur for high state of cure.

Accelerator combinations is used because of the low solubility of the polar accelerators in the unpolar elastomer – less effective and bloom.

<b><u>Accelerator</u></b>	<b><u>Sol. Limit (phr)</u></b>	<b><u>Accelerator</u></b>	<b><u>Sol. Limit (phr)</u></b>
CuDMC	0.3	ZDBC	2.0
TeDMC			
TMTD	0.5 – 0.7	CBS	2.5
TMTD		MBS	
ZDMC		TBBS	
DTDM	0.7 – 0.9	MBT	3.0
TETD		MBTS	
ZDEC			

- Solubility drops with increasing ethylene content
- Naphthenic oil is better than paraffinic oil for improved solubility
- Stearic acid has a slight solubilizing effect

# Peroxides

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Bloom does not occur with most peroxides.

But two decomposition products of Bis-(tert-butylperoxyisopropyl)-benzene may cause bloom.

The chemicals responsible for a whitish dry bloom are the high molecular alcohols m- and p-dihydroxyl diisopropyl benzene.

The other decomposition products are either rubber soluble or volatile such as acetone and methane.

# Plasticizers

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Compatibility between the plasticizer/oil and the elastomers mainly governs the tendency for bloom.

e.g. 2phr **paraffinic oil** in NBR vulcanizate can result in an undesirable greasy surface due to excessive bleeding of the plasticizer.

Similarly, 5phr **paraffinic oil** can bloom (exude) heavily from CR vulcanizate.

**Naphthenic oil** can be used in CR at 20-25phr without bloom problems.

**Aromatic oils** are very compatible with CR. However, high level Ar.Oil may cause sticking to equipment. Stickiness is much reduced by adding some naphthenic oil that have a certain lubricating effect.

Waxes, petroleum jelly, blown asphalt and coal tar can reduce the compatibility of oil in CR.

**Antistatic plasticizers** are known to cause heavy bloom when used above their solubility limit. In the case for silica filled compound with antistatic plasticizer, undesirable bleeding can be avoided by eliminating DEG which is often used as an activator in the formulation.

# Antidegradants

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## ***Anti-ozonants***

- Must react with ozone faster than the elastomer
- Must be available at the vulcanisate surface
- The reaction product with ozone (ozonide) must form a continuous protection film against further ozone attack.

When totally soluble material is used the surface concentration will be proportional to the dosage level and not change on storage.

The faster and the higher the surface concentration, the more effective the anti-ozonants. The ranking as follows:-

IPPD (N-isopropyl-N'-phenyl-p-phenylenediamine)

DTPD (N,N'-Ditolyl-p-phenylenediamine)

6PPD (N-1,3-dimethyl butyl-N'-p-phenylenediamine)

77PD (N,N'-Bis-(1,4-dimethyl pentyl)-p-phenylenediamine)

## Antidegradants (cont')

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### ***Anti-oxidants***

Blooming generally does not occur with phenolic and phosphite antioxidants which have high solubility limit in rubber.

PBN which was widely used in former times, caused bloom at over 1.5 – 2phr.

PAN might be used up to 5phr without bloom.

Polymerized 2,2,4-Trimethyl-1,2-dihydroquinoline (TMQ) migrates to the surface of uncured carbon black filled compound and causes a color change from black to dark blue after stored for a period of several days.

The oligomers present in TMQ at concentrations depending upon the production process have a higher solubility in rubber than the polymeric substance. The blooming rate is shown as below:-

Polymeric TMQ > Tetramer > Trimer > Dimer > Monomer

More than 1000 components have been detected in TMQ. Impurities of that kind have the tendency to revert insoluble sulphur to soluble type and for subsequent sulphur bloom.

# Retarders

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Acid type retarders like ***Phthalic anhydride (PTA)*** and ***Salicylic acid*** ***or*** ***N-phenyl-N-(trichloromethyl-sulphenyl)-benzene sulphonamide*** give no blooming so far.

***Benzoic acid*** (not only as retarder but also as viscosity reducer, and at high dosage to increase hardness) can migrate to vulcanizate surface.  
-- transparent to whitish crystals like frost pattern on window pane on steam cured vulcanizate.

***Cyclohexylthiophthalimide (CTP)*** can cause a grayish bloom at above 0.4 to 0.5 phr.

# Lubricants

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## ***Zinc Soaps***

Zinc stearate and most linear saturated fatty acids based zinc soaps have very low solubility in rubber.

Zinc stearate can only be observed when the vulcanizate is slowly cooled and diffusion to the rubber surface can take place.

Nevertheless, amines as accelerator decomposition products will complex and solubilize the zinc, thus zinc stearate does not appear at the vulcanizate surface. But when in contact with water vapor, insoluble basic zinc stearate can be formed and bloom out.

Zinc soaps of branched or aromatic carboxylic acids are soluble in rubber. They provide substantial improvement in creep and modulus reproducibility compared with zinc stearate.

## ***Fatty Acid Amides***

Very limited solubility in this group of lubricants which bloom easily to provide anti-block properties for polyolefin films at dosage of just 0.05%.  
-typical e.g. are amides derived from stearic, oleic and erucic acid.

# Resorcinol

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Resorcinol has limited solubility in rubber so it blooms. Its tendency of bloom increases in presence of Hexamethylene tetramine (HMT).

A non-blooming derivative of resorcinol is available to users of RFS (Resorcinol/Formaldehyde/Silica) adhesive system.

# Fillers

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Fillers are insoluble and cannot migrate.

In some cases, the exposure of fillers at vulcanizate surface is actually termed as "Frosting".

Frosting is caused by ozone attack and also ultra-violet degradation on relaxed vulcanizate containing white fillers. Usually the frost is of white or gray color.

Very often, frosting is mistaken as bloom by un-reacted accelerators and etc. But frosting is confirmed as solvent washing or heating would not remove the "bloom layer".

Optimum filler dispersion will help to avoid frosting.

# Colorants

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Organic colorants which are not completely soluble can cause crystalline bloom.

Inorganic colorants are insoluble and thus no bloom is generated.

“Plate Out” of colorants are known from plastic processing is caused by insufficient compatibility of certain additives, such as plasticizers or lubricants. Exudation of these additives take place on processing and part of the colorant is transported by the additive to the surface.

Plate out can also occur with fillers.

Plate out deposits on calender bowls and extruder dies.

# SUMMARY

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This presentation does not really totally help you how to eliminate or solve the blooming problem  
BUT at least guide you how to prevent the tendency to occur.

The concept of  
***PREVENTION IS BETTER THAN CURE***  
is applied.