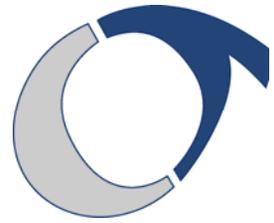


CHEM TECHNOLOGIES, LTD.

Beyond the obvious from innovation to application



Dispersions for Environmental and Safety Improvements

Environmentally Safe

Economical

Exposure-less

Easy to Use

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Dispersion Technology Conference

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The 4-E's of Dispersions



1. ***E*Environmentally Safer**
2. ***E*conomical**
3. ***E*xposure-less**
4. ***E*asy to use**

Background



- **Environmental and safety concerns with rubber and plastic additives have come to the fore front recently.**
- **General Motors and other car manufacturers have issued new IMDS (International Material Data System) standards requiring certain chemicals with health risks to be reported including nitrosamines, skin sensitizers, cancer suspect chemicals, heavy metals, and chemicals that pose health risks.**
- **Other US based car companies are indicating that they will follow this lead.**
- **This paper will talk about how the use of dispersions in pre-weighed batch inclusive bags can reduce environmental and safety concerns of using chemicals.**

Chemicals in the Rubber Industry With Environmental/Safety Concerns



- **Carcinogens and suspected carcinogens**
- **Heavy metal containing chemicals**
- **Skin sensitizers**
- **Skin, eye and respiratory irritants**
- **Corrosive chemicals**
- **Inhalation hazardous chemicals**
- **Chemicals with physical hazards**
- **Environmentally hazardous chemical disposal**

Carcinogens & Suspected Carcinogens



- **Accelerators & other rubber chemicals that can form carcinogenic nitrosamines**
- **Sulfenamides and thiazoles – these accelerators generate 2-mercatobenzothiazole (MBT) as the active curative and also have small amounts of free MBT present. MBT was put on the Section 313 list because NTP has it listed as a suspect cancer causing substance.**
- **DOTG (diorthotolyl guanidine) – DOTG contains up to 1% orthotoluidine which listed by IARC as a Group 2B possible human carcinogen.**
- **Clays & Talc – may contain some crystalline silica (quartz) which IARC & NTP classifies as a Group 1 carcinogen when inhaled.**
- **Aromatic Oils - classified as a Group 1 (proven human carcinogen) by IARC.**
- **Antimony Oxide – classified as a IARC Group 2B carcinogen**
- **N-phenyl-1-naphthylamine (PANA) – an antioxidant that is a cancer suspect.**
- **Phenol-formaldehyde, Methylated melamine-formaldehyde (HMMM) and Resorcinol-formaldehyde Resins – can contain residual amounts of phenol (IARC Group 3 suspected carcinogen) and formaldehyde (Group 2A - IARC and NTP Group 2, OSHA – suspected).**
- **Carbon Black - Group 2B possible human carcinogen (IARC)**
- **Ethylene Thiourea (ETU) - Reasonably Anticipated (NRC)**

Heavy Metal Containing Materials



- **Heavy metals are now being watched for both environmental and health issues.**
- **Some of the health issues with heavy metals are:**
 - **Cancer**
 - **Nervous system damage**
 - **Inhalation poisons**
- **Some of the materials in the rubber industry containing heavy metals are:**
 - **Antimony Oxide (filler) – contains lead, arsenic and antimony**
 - **Chromium Compounds (colorants)**
 - **Copper Compounds (CDMC, CMBT, CDBC accelerators)**
 - **Nickel Compounds (NDBC) accelerator, antidegradant**
 - **Tellurium (TDEC accelerator)**
 - **Iron (colorant)**
 - **Titanium Dioxide – contains titanium**
 - **Zinc Oxide – contains zinc and residual amounts of lead**
 - **Zinc Compounds – (zinc accelerators such as ZMBT, ZDMC, ZDBC, ZBEC, zinc stearate, zinc containing slabs dips, zinc oxide and many other zinc containing compounds)**

Skin Sensitizers



- **Skin sensitizers are chemicals that can cause an immediate allergic reaction and/or sensitization over time.**
- **Skin sensitizers automatically get a 2 rating on the HMIS scale (moderate health risk).**
- **Chemicals that are skin sensitizers are quite common in the rubber industry. They include:**
 - **Thiazole accelerators – MBTS, MBT**
 - **P-Phenylene diamine antidegradants – 6PPD, DPPD, IPPD, etc.**
 - **Azodicarbonamide foaming agents**
 - **Trifunctional acrylic esters**
 - **Hexamethylenetetramine (HMT) – methylene donor**
 - **Resorcinol and resorcinol –formaldehyde resins – adhesion promoter**
 - **Thiourea accelerators**
 - **Some thiuram and dithiocarbamate accelerators – can cause sensitization and/or a temporary allergic reaction if alcohol is consumed before or after handling.**

Skin, Eye & Respiratory Irritants



- **Just about every chemical used in the rubber and plastics industry can fall under the irritant category.**
- **Some individuals are more susceptible to irritants than others.**
- **Over exposure to chemical irritants over time can cause allergic reactions and sensitization.**

Corrosive Chemicals



- **Many chemicals can cause severe skin burns, eye ulceration and respiratory damage.**
- **Usually these chemicals have a HMIS health rating of 3 (serious hazard).**
- **Below are just a few of these chemicals:**
 - **Calcium oxide (a desiccant) that can cause skin burns.**
 - **Resorcinol and resorcinol based resins which can cause skin burns.**
 - **1,8-Diazabicyclo-5,4,0-undecene-7 (DBU)**
 - **zinc-O,O-di-n-butylphosphorodithioate (ZBPD)**
 - **m-phenylenedimaleimide**

Inhalation Hazards



- **Many chemicals used in the rubber industry are hazardous by inhalation:**
 - **Highly toxic by inhalation – accelerators CDMC, ZDMC, TDEC**
 - **Toxic by inhalation – TBzTD, antimony oxide, fumed silica, alkylated melamine-formaldehyde resin (HMMM)**
 - **Other inhalation hazards – amorphous silica, talc, clays, zinc oxide**
 - **Any chemicals that produce dust that can be inhaled can be considered potential inhalation hazards. This includes the vast majority of the rubber chemicals.**

Physical Hazards



- **Most organic rubber chemicals can form explosive dust/air mixtures in dusty plant environments.**
- **Flammable solids such as sulfur, p,p'-oxybis(benzene sulfonylhydrazide) [OBSH], azodicarbonamide.**
- **Flammable liquids**
- **Liquids that are used in small amounts that have to be heated and weighed by hand.**

Environmentally Hazardous



- **Most sulfenamides, thiazoles, guanidines, thiurams and some dithiocarbamates accelerators are IMDG Class 9 environmentally hazardous materials, toxic to aquatic organisms.**
- **Heavy metal compounds (Te, Zn, Cu, Ni, etc.) such as TDEC, ZBEC, CDMC, zinc oxide are hazardous waste per the Superfund law 40 CFR 302.4 and Section 313 Toxic Chemicals 40 CFR 372.65**
- **Thiurams are particularly hazardous to aquatic organisms and many are classified by DOT as marine pollutants.**

Hazardous Waste Chemicals



- This is just a sample of some of the hazardous waste chemicals.
- Many rubber additives contains small amounts of hazardous waste chemicals that would cause them to be classified as hazardous for disposal.
- Individual state and local laws may also classify certain chemicals as hazardous.

RCRA Wastes (D, P, U, F/K, or Appendix VIII lists)	SARA Title III Section 313 Toxic Chemicals	Superfund Reportable Quantity Chemicals
TMTD	TMTD	TMTD, 10 lb.
Diethylhexyl phthalate	MBT	
ZDMC	heavy metal compounds	heavy metal compounds
Diphenylamine	Diethylhexyl phthalate	Diethylhexyl phthalate, 100 lb
ETU	ZDMC	ZDMC, 1 lb.
AZO	Diphenylamine	OBSH, 100 lb.
Phthalic anhydride	Antimony oxide	Resorcinol, 5000 lb.
Dibutyl phthalate	Glycol ether compounds	Antimony oxide, 1000 lb.
	ETU	Glycol ether compounds
	AZO	ETU, 10 lb.
	Phthalic anhydride	Phthalic anhydride, 5000 lb.
	Ethylene glycol	Ethylene glycol, 5000 lb.
	Dibutyl phthalate	Dibutyl phthalate, 10 lb.

Exposure-less Cure Systems



- **With the new focus on environmental issues and less exposure of plant workers to chemicals, purchasing dispersions in pre-weighed batch inclusive bags becomes more attractive.**
- **There are advantages in using not only pre-weighed chemicals but using multi-ingredient dispersions of the rubber chemicals.**
- **Most organic rubber chemicals show a slight eutectic reaction when they are combined together with a small amount of plasticizer that is compatible with rubber compound.**
- **Multi-ingredient dispersions disperse quicker and more thoroughly in the rubber compound allowing for economic advantages including a better final product.**

Advantages of Dispersions:

Economics

Quality

Environment

Health & Safety

...from raw materials to

... finished goods

Purchasing



Reduced number of materials to be purchased:

- **Time savings for purchasing agents**
- **More efficient sourcing**
- **Reduced incoming freight costs**
- **Reduced number of invoices & other paperwork**
- **A custom blender such as Chem Technologies buys truckload/skid quantities of chemicals with economical high volume pricing**
- **Reduced number of suppliers & items purchased allowing for closer control over quality issues such as CpKs, etc.**

Economics

Quality

Inventory



Reduced inventory resulting in:

- **Reduced complexity – greatly reduced number of individual raw material codes allowing for:**
 - ❖ **Simpler more efficient warehouse**
 - ❖ **Easier tracking of first in – first out inventory of materials**
- **Reduced labor**
- **Increased warehouse space, returnable containers can be stacked 5 containers high.**
- **Less traffic and congestion on receiving docks**
- **Reduced tow motor traffic**
- **Reduced waste from disposing of:**
 - ❖ **Out-of-date infrequently used chemicals**
 - ❖ **Partially opened bags that have been exposed to moisture & air**

Raw Material Maintenance



Reduced number of coded materials resulting in:

- Reduced laboratory testing
- Reduced number of MSDS to file
- Reduced incoming certificates of analysis to review & file
- Reduced number of raw material specifications to maintain for quality reporting

Fresher materials

- Many rubber chemicals such as accelerators & antidegradants degrade when exposed to moisture, air and high summer temperatures.
- Preweighed dispersion blends greatly reduce this aging process because they are sealed in polybags until they are used in the mixer.
- Some rubber chemicals are used in small amounts and they may exceed their shelf-life before they are consumed. Custom dispersion blenders use large amounts of rubber chemicals and have a greater turn-over of chemicals resulting in fresher chemicals to the customer.

Packaging



- **Most rubber chemicals come in some type of disposable packaging such as paper bags, polybags, cardboard boxes, etc. loaded onto wooden or cardboard skids. When the chemicals are consumed the packaging has to be disposed of.**
- **Dispersions come in preweighed batch inclusive low melt polybags which can be thrown directly into the mixer.**
- **The individual preweighed dispersion bags can be packaged in returnable containers that require no pallets.**
- **Rubber chemicals that come in powders can leave up to 1/4 of a pound of residue in the empty bag which results in both economical and environmental concerns.**

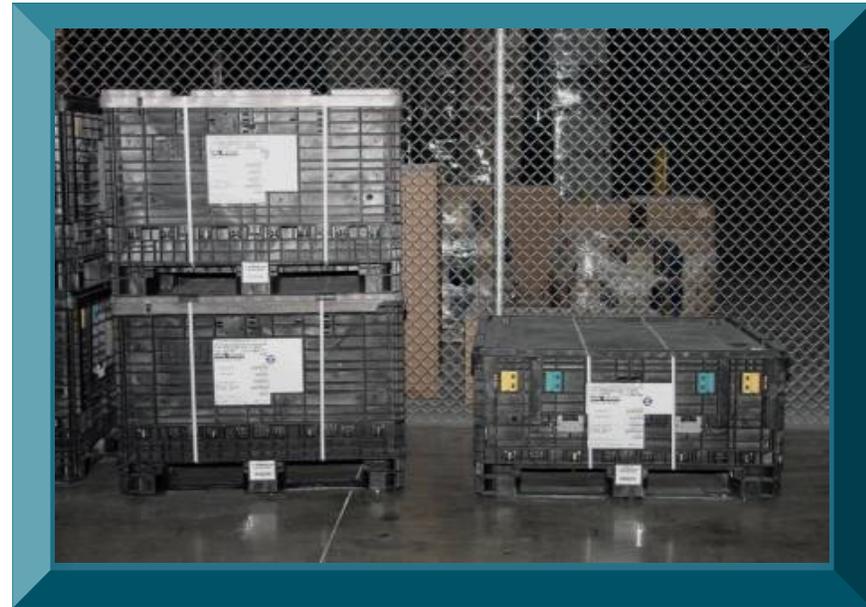
Dispersion Packaging



**Preblends in batch inclusive bags
in traditional corrugated packaging**



**Alternative environmentally friendly
returnable containers**



Compound Staging Area



- **The common rubber formulation has around 15 individual materials. Materials such as carbon black, oil, etc. are typically fed to the internal mixer automatically. However, the remaining ingredients must be weighed up by a compounder.**
- **Our multi-ingredient preblend dispersions have an average of 7 ingredients but some have up to 15 ingredients. Use of preblend dispersions has the potential to simplify or even eliminate the compounding area resulting in:**
 - **Reduced labor costs**
 - **Reduced weighing errors**
 - **Reduced floor space**
 - **Less congestion in the mixing/compounding area**
 - **Reduced tow motors**
 - **Reduced number of scales to calibrate and maintain**
 - **Reduced physical labor – handling preweighed packages that weigh from 5 to 20 lb. instead of 50-55 lb bags of powdered materials.**
 - **Reduced contact of workers to rubber chemicals that are commonly skin sensitizers, inhalation hazards, potential cancer hazards, etc.**
 - **Cleaner, safer work environment**

Mixing



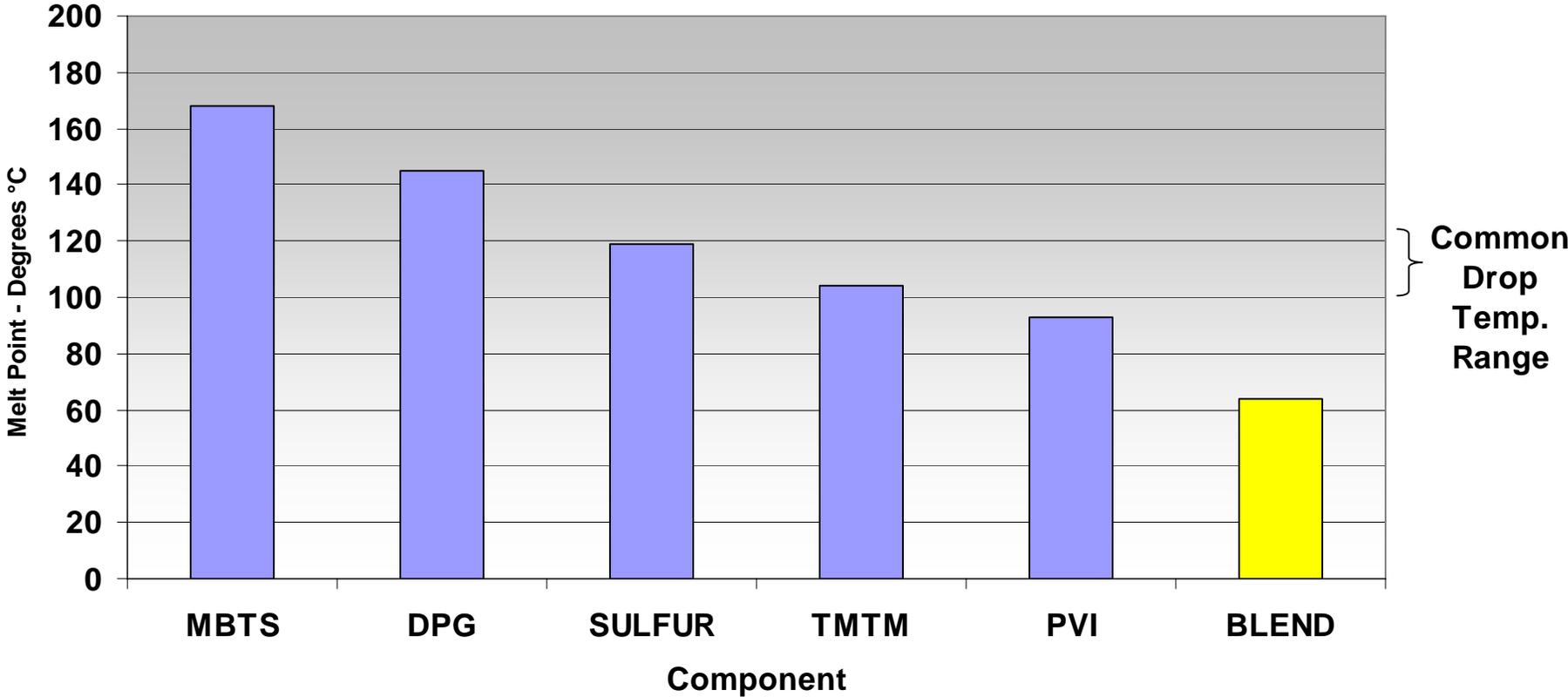
- **Blended dispersions in pre-weighed bags are added directly to the internal mixer. There is virtually no loss of chemicals from spillage on the feed belt or up the dust collection system. The blended chemicals have a lower melt point than the individual ingredients allowing for faster & more homogeneous mixes. This results in:**

- **Faster & lower temperature mixing**
- **Possibility of reduction of a 2 or 3 pass mix to a single pass mix**
- **Lower energy consumption**
- **Less wear & tear on the internal mixers**
- **More floor space around the mixer**
- **Reduced physical labor by the operator**
- **Better batch to batch consistency with tighter rheometer specs.**
- **No loss of chemicals from dust & better dispersion results in the potential to reduce the amount of chemicals used.**
- **Reduced contact of workers to rubber chemicals that are commonly skin sensitizers, inhalation hazards, potential cancer hazards, etc.**
- **Cleaner, safer work environment**

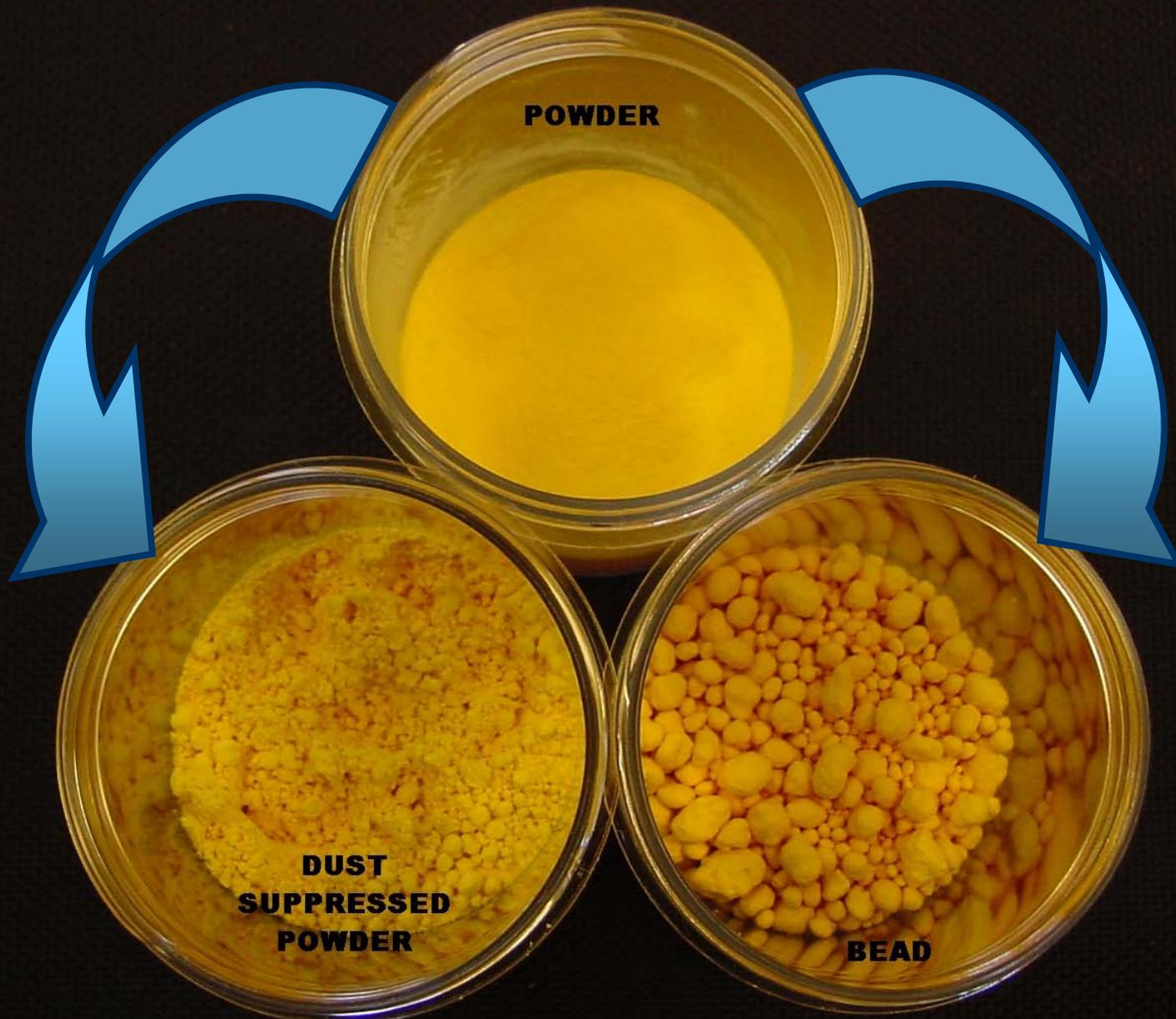


This graph shows that curatives combined in a dispersion lowers the overall melt to below the mixer drop temperature of rubber compound allowing for a melting dispersion into the rubber as opposed to a mechanical dispersion as would be the case with the higher melting point accelerators such as MBTS.

**Multiple Ingredient Blend
Initial Melt Point Comparison**



FROM DUSTY POWDER TO ...



DUST SUPPRESSED POWDER *or* DUST FREE BEAD

Mill Incorporation Study

100% Active Powder Blend

90% Active Dust Suppressed Powder Blend Dispersion

80% Active Bead Blend Dispersion

**80% Active Single Ingredient Polymer Bound
Dispersion**

Incorporation Times



- **100% active powder blend**
4:10
- **90% active dust suppressed powder blend dispersion**
0:45
- **80% active dust suppressed bead blend dispersion**
0:35
- **80% active polymer bound single ingredient dispersion**
0:40

Processing Lines – Extrusion, Molding, Calendering, Etc.



- **The use of preblended dispersions results in a more consistent, more homogenous compound from the mixer which in turn results in more consistent product from the processing lines:**
 - **May allow for faster processing**
 - **Less scrap**
 - **More consistent die swell**

Economics

Quality



- **Preblended dispersions allow for:**
 - Reduced number of raw materials in the plant
 - Reduced air-borne dust
 - Reduced worker contact with chemicals
 - Less loss of chemicals allowing for reduced chemical usage
- **Most preblended dispersions are treated which typically reduces the chemicals health hazards.**
 - For example ZDMC (zinc dimethyldithiocarbamate) is a severe inhalation hazard in the untreated powder form. After treatment in our blends, the inhalation potential of ZDMC is reduced because it is in a form (larger particle size) that is no longer regulated because it cannot be inhaled.
 - Another example is sulfur, a flammable solid. Once sulfur has been mixed into our treated blends it is no longer a flammable solid.
- **The net results of the above allows for less regulatory reporting & potentially healthier work force.**

Finished Goods



- **Because of their advantages, preblended dispersions are often used in products that require fine tolerances, high physical properties & excellent appearances such as:**
 - **Extruded profile weather stripping**
 - **Wire & cable jackets**
 - **Vibration control parts**
 - **O-rings**
 - **Pharmaceutical goods**
 - **V-belts**
 - **Hoses**
 - **Tires**
 - **Other high-tech molded & extruded rubber goods**

Quality Advantages

Reduced Chemical Usage



- ***Purchasing*** - Reduced number of suppliers & items purchased allowing for closer control over quality issues such as CpKs, etc.
- ***Raw Material Maintenance*** – Fresher materials because preblends come in sealed batch inclusive bags that are a barrier to moisture.
- ***Compound Staging Area*** – Fewer raw materials allowing for fewer weigh-up errors.
- ***Mixing*** – Faster mix cycles, reduced energy consumption. Faster and better dispersion into the compound is often the result of the effect of a lower melt point when the chemicals are mixed together with a binder.
- ***Processing*** - The use of preblended dispersions results in a more consistent, more homogenous compound from the mixer which in turn results in more consistent product from the processing lines. Batch to batch consistency is also dramatically improved.
- ***Final Product*** – Better appearance, high quality and less scrap.
- ***Overall*** - The net result of the above advantages is an overall reduction in the amount of chemicals used and a higher quality finished product.



- **Preblended dispersions can:**
 - **Improve the overall economics of your plant**
 - **Reduce complexity of your plant**
 - **Improve health & safety of your workers**
 - **Reduce regulatory tracking (SARA)**
 - **Improve the appearance of the compounding & mixing areas of your plant**
 - **Improve the overall quality of your finished goods**