

Green colour carriers for PU soles

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Pigment dispersions are the most common way to add colour to polyurethane elastomers and phthalate plasticisers, the carrier used. Unfortunately, phthalates are endochrines which can be harmful to the body (especially children) and, as a result, are likely to become subject to strict legislation in the future. There is an urgent need to find an equal and economical alternative, so REPI has carried out a programme of laboratory tests to compare the performance of conventional phthalate-based dispersions with a range potential 'green' carriers.

Phthalate plasticisers have been popular due to the fact that their very low viscosity combined with a suitable dispersing agent allows a good addition and dispersion of colour pigments over a viscosity range of 500-2500 cps (centipoise or metric unit of dynamic viscosity) at 20°C. This low viscosity makes the dispersion method particularly suitable for direct dosing into the mixing head on standard casting machines. Direct injection machines need a slightly higher viscosity and this can also be achieved by simply reformulating the dispersion.

Furthermore, phthalates have provided a cost effective method that also maintains a high level of quality provided the correct phthalate carrier is chosen. They are also inert components, so no particular formulation adjustments are necessary, which makes them easy to use.

PHthalates and REACH

Recent years have seen increasing concern regarding the toxicity of certain phthalates. Some are now considered unacceptable and a number of companies have begun to avoid these types of products fearing that sooner or later all phthalates could be banned.

The major drivers that have led REPI to develop an effective alternative have included improving environmental aspects and REACH (Registration, Evaluation and



Authorization of Chemicals) requirements. REACH is a system created in the EU to monitor chemical products throughout their life cycle. In addition, there will soon also be GHS (Global Harmonised System) in place to examine all Substances of Very High Concern (SVHCs).

VEGETABLE OIL BASED DISPERSIONS

The meaning of the expression 'green' has been exhaustively covered already in various articles and publications and many meanings have been listed. Our definition is 'materials derived from natural products that reduce the use of petroleum-based raw materials and, in the end,

result in less global emissions'. REPI has succeeded in developing two lines of green colours. While one is still based on a phthalate-free plasticiser, the other is based on vegetable oil (BIO).

The major chemical difference between using a vegetable oil-based carrier rather than a phthalate is represented by the presence of OH (hydroxyl radical*) groups that can vary with the type of oil used and so merely require small formulation adjustments. The molecular weight of vegetable oil is also higher than that of phthalate plasticiser, so VOC (volatile organic compounds as defined by the EC Solvents Emissions Directive) emissions are minimal.

DEVELOPMENT

These BIO-based dispersions required specific chemical developments in order to create the three main colour groups – black, white and the full range of all other colours. Black and white comprise the largest volume used in PU footwear either as single products or when blended with primary colours to create specific shades.

While REPI as a manufacturer of pigment dispersions needs to cover the entire colour range, the greatest attention

Figure 1: UV TESTS

CIE LAB	REFERENCE	50 h UV EXPOSURE (SUN TEST)	
		BIO BASED	PHTHALIC PLASTICISER
L	62.51	75.83	77.7
a	-0.66	-1.75	-1.93
b	-0.56	15.77	17.31
Yellow index (db)		16.33	17.86

was initially paid to black. This is not only the most frequently used colour but is often also the most critical pigment as the right choice of carbon black is essential in maintaining all the various grades of black that are involved. These grades must all be pourable and pumpable whatever the various carbon black concentrations.

White pigment dispersions, on the other hand, generally have a higher viscosity. The level of titanium dioxide used to produce white pigment can be as high as 70% of the total formulation while still maintaining good flow characteristics. Having successfully formulated black and white, the development of a full colour range presented few extra problems and the same ample range of shades available in phthalates is now also available BIO-based.

One particular challenge that did arise was when UV stabiliser blends were incorporated in the same formulation of pigment dispersion. The table in Figure 1 shows the comparative results obtained from exposing a UV stabilised phthalate-based white dispersion and a BIO-based version.

The important value to note is the Yellow Index where the Bio-based dispersion is shown to give a slightly better performance compared to the phthalate version.

PERFORMANCE

Shoe soles coloured with BIO-based products have been evaluated for physical mechanical properties. Figure 2 shows

Figure 2: EVALUATION OF VEGETABLE OIL BASED BLACK

Test	Neutral	Black 99350	Black 99672
Addition rate %		3%	3%
Hardness ShA° after hydrolysis 7 days	44 44	44 45	45 42
Tensile Strength (N/mm ²) after hydrolysis 7 days	5.6 5.8	5.7 5.7	4.8 5
Elongation at break (%) after hydrolysis 7 days	394 419	391 428	365 406
Flex test 30 kC thick 8 mm (mm) after hydrolysis 7 days	3.3 2	2.8 2	2.4 2
Tear strength (N/mm)	4.7	4.6	5
Abrasion (mg)	141	224	51
Loss of Hardness 7 days	0	0	0
Tensile Strength Retention 7 days	104%	100%	104%

typical values under hydrolytic ageing conditions where no significant differences are noticed with the ester formulation. Abrasion resistance results did however show a dramatic improvement.

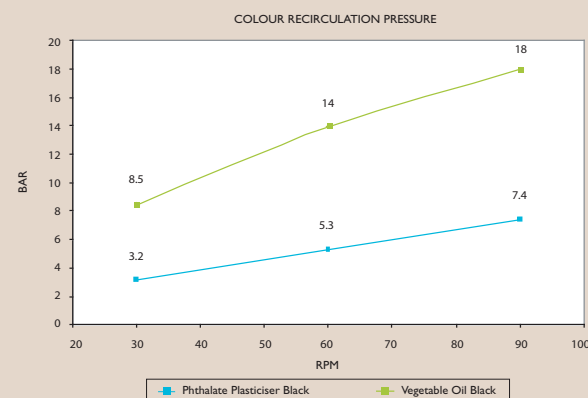
As PU-soled shoes are used in many different work environments, a particularly difficult one, automotive, was selected, where specifications on fogging emissions are tight and VOC must be held below 200 ppm (parts per million).

The test safety shoes passed VW, BMW and Mercedes fogging tests. Black Remap paste in fact showed 47 ppm when this dispersion was used at 3% addition to the polyol, the total emission contribution being just 1ppm.

PROCESSABILITY

It is important to keep a stable pressure in the colour circuit of a direct injection machine for PU footwear. Here, viscosity plays a key role. BIO-based dispersions have a viscosity of around 4000 cps so the pressure needed in the circuit has to be double that of a standard phthalate of 2000 cps. That in turn is equal to the pressure of the main components, which results in reduced turbulence when the colour meets the polyol and isocyanate components in the mixing head. This is perhaps best explained by a graph (Figure 3).

Figure 3: PROCESSABILITY



BIO-based colour dispersions offer a number of advantages to footwear manufacturers. They can be used with both polyether and polyester systems on conventional dosing equipment. They improve material flow characteristics and create a good foam structure. They are easy to store and handle. They are also free from harmful phthalate carriers, non-toxic, derived from a renewable raw material resource and are environmentally friendly.

In the steady 'greening' of industry, they can help the footwear industry in particular to play its part. 🌱

* Radicals (or free radicals) are atoms, molecules or ions with unpaired electrons. These are usually highly reactive and so form an important part in many chemical reactions.



DESMA TPU processing unit. ALL CREDITS: DESMA

Innovative colour dosing for TPU

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The market trend towards 'Mass Customisation' for almost all consumer goods means bigger ranges, smaller unit volumes and higher production costs. This has created problems for footwear manufacturers using direct injection moulding systems where the larger the volume, the greater the efficiency. The process of colouring TPU for this type of soling construction is one of the most expensive processes in modern shoemaking, so a way to speed it up and reduce waste would be a welcome development.

The new DESflow TPU colour dosing unit has been developed to do just that. It overcomes these problems by injecting liquid colour into the TPU during the plasticising phase immediately prior to the mould being filled and removing the need for pre-coloured granules. Quantity is metered at a constant percentage and up to four different colours can be interchanged. It also offers good material distribution within the mould cavity, optimal colouring of the finished sole and considerable cost savings:

- One neutral colour base TPU stock as against four separate ones
- Five to ten minute colour changes rather than 15 to 60 minutes
- 0.5-4.5kg waste per colour change compared to 10-50kg

TPU TECHNOLOGY

The standard DESMA injection system is the DESflow process shown in the header image. It works by pouring hot liquid TPU on the bottom plate of the mould cavity and then pressing it into the edges of the mould. This avoids the use

of runner channels which can create frictional heat and affect the heat-sensitive TPU compound. It also reduces the amount of waste they create as well as the clamping required, making it possible to use cheaper aluminium moulds. Flow marks are also lessened due to the improved pre-distribution of material within the mould.



Casting by the DESflow process.

PROCESSING COLOURS

The traditional method has been to use pre-coloured granules for direct processing on the machine without any further additive. This involves buying in pre-mixed masterbatches from a supplier or making them in-house with tumbler or big mixing bins. A more recent improvement has been to colour the material directly at the machine with either solid or liquid colours, using different types of pump.

Colour intensity depends on the amount of pigment added and the amount of additional colour, and on the type