Clariant

Impact of stabilizers on the color of pigmented polymer articles

AMI – MASTERBATCH 2002

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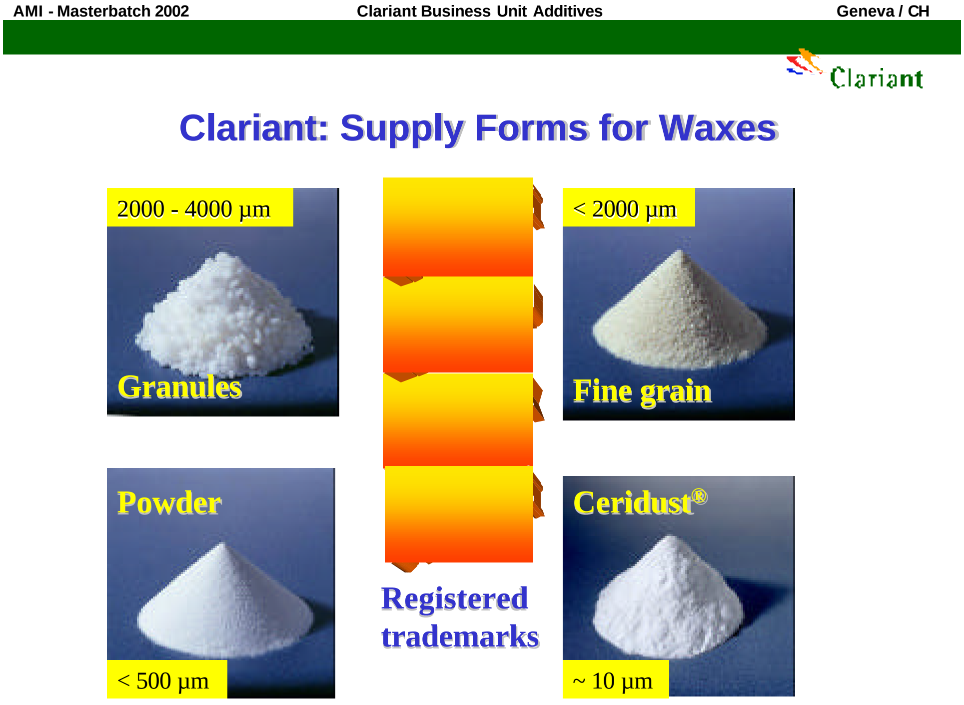
1 Introduction

Huge amounts of expensive pigments are used by the masterbatch industry to produce finally colourful products. Enormous efforts are made to achieve exactly the desired shade. Doing this in an economical way is a prerequisite to be successful. The first part of the presentation deals with the pigment dispersion, which has a direct impact on the pigment masterbatch costs. In the further parts interactions between stabilisers and pigments were discussed, which can lead to undesired colour variations - costly and time consuming experiments can be the consequence.

The impact of stabilisers - or additives in general - on the colour of pigmented polymer articles will be discusses in three chapters:
1. Pigment dispersion
2. Direct impact of additives on the colour
3. Long time effects during usage of the product.

In all three stages there can be positive and negative impacts of the additives on the colour. The positive impacts lead to a more economical way of colouring the final product. This can be e.g. due to an improved pigment dispersion or another positive interaction between pigment and additive resulting in a better colour yield or overall better stability of the whole article.
On the other hand the interactions between pigments and additives can be negative as well, worsening the pigment dispersion or leading to a discolouration e.g. of the additives themselves. A decreased stability of the final product is a further aspect.

2 Improved pigment dispersion with waxes:



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Clariant: Supply Forms for Waxes

2000 - 4000 µm
Granules

< 2000 µm
Fine grain

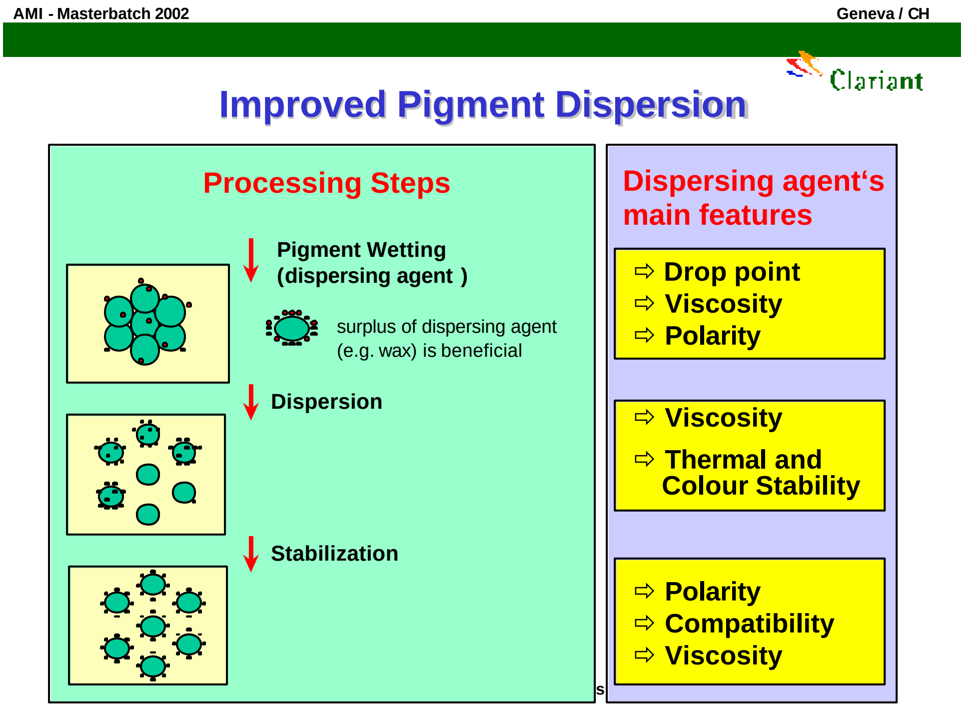
Powder
< 500 µm

Ceridust®
~ 10 µm

Registered trademarks

Fig.2: Physical forms and tradenames of Clariant Waxes

Dispersing pigments into polyolefins , various physical forms of –mainly- Clariant's polyolefin waxes and new metallocene waxes have been used: this gives an overview over the particle sizes related to these physical forms: waxes have been used from particle sizes of 2000 µm down to particle sizes of 5µm – with very different effects.



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Improved Pigment Dispersion

Processing Steps

Pigment Wetting (dispersing agent)

surplus of dispersing agent (e.g. wax) is beneficial

Dispersion

Stabilization

Dispersing agent's main features

- ⇨ Drop point
- ⇨ Viscosity
- ⇨ Polarity

- ⇨ Viscosity
- ⇨ Thermal and Colour Stability

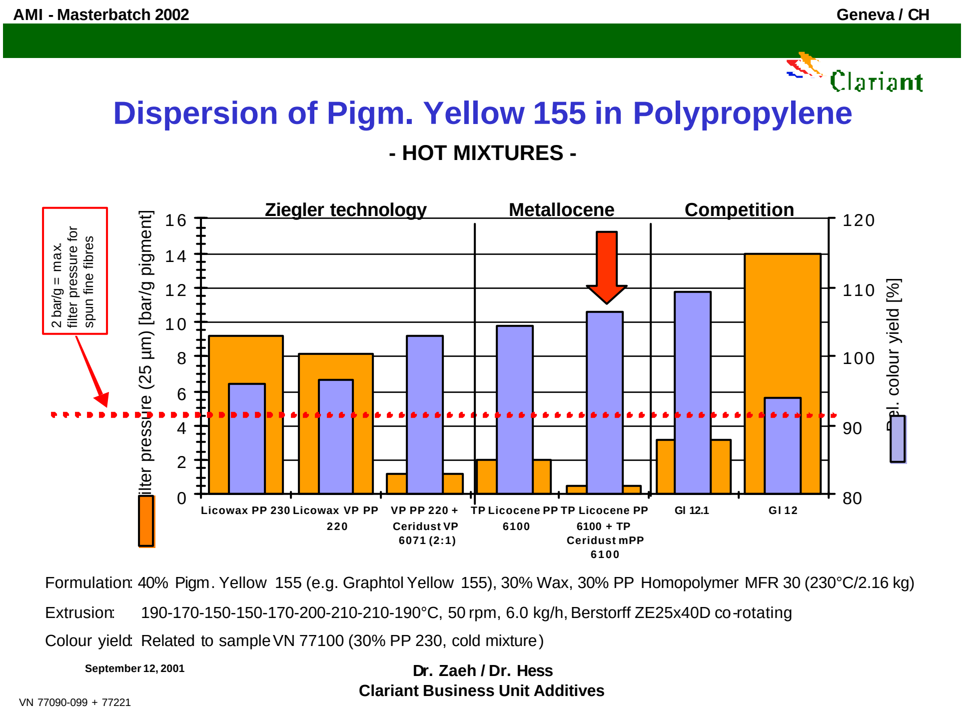
- ⇨ Polarity
- ⇨ Compatibility
- ⇨ Viscosity

Fig. 3: Steps for dispersing a pigment into a polymer matrix

If we try to analyze the steps needed for the dispersion of a pigment into the respective polymer matrix , there is a significant difference regarding the profile of the “best choice” dispersing additive for each step:

- Whereas the ideal dispersant would be low-viscous , polar and highly surface-active for the first step , the **wetting of the pigment agglomerate** , this looks different for the steps to come.
- During the shear process , **taking the pigment agglomerates apart** , the ideal dispersing additive is bringing more shear to the process , i.e. it is highly viscous, low or no functional and of excellent thermal stability.
- In the final step , **anchoring the pigment into the polymer matrix ,** again compatibility , i.e. no functionality and ideally a “fit-to-the-polymer” would make the dispersant work well.

This simple comparison brings to light , that there is basically no ideal dispersant regarding all the major needs of pigment dispersion into polymer matrices , specially if one thinks further about the major differences in pigment functionality and all the polymer matrices being chosen for pigment masterbatches. In other words , there is no “stone of wisdom” dispersant fitting all needs and all purposes: we will for this talk have a look at some pigment examples (organic and inorganic) and polypropylene as polymer carrier material.



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Dispersion of Pigm. Yellow 155 in Polypropylene

- HOT MIXTURES -

Formulation: 40% Pigm. Yellow 155 (e.g. Graphtol Yellow 155), 30% Wax, 30% PP Homopolymer MFR 30 (230°C/2.16 kg)

Extrusion: 190-170-150-150-170-200-210-210-190°C, 50 rpm, 6.0 kg/h, Berstorff ZE25x40D co-rotating

Colour yield: Related to sample VN 77100 (30% PP 230, cold mixture)

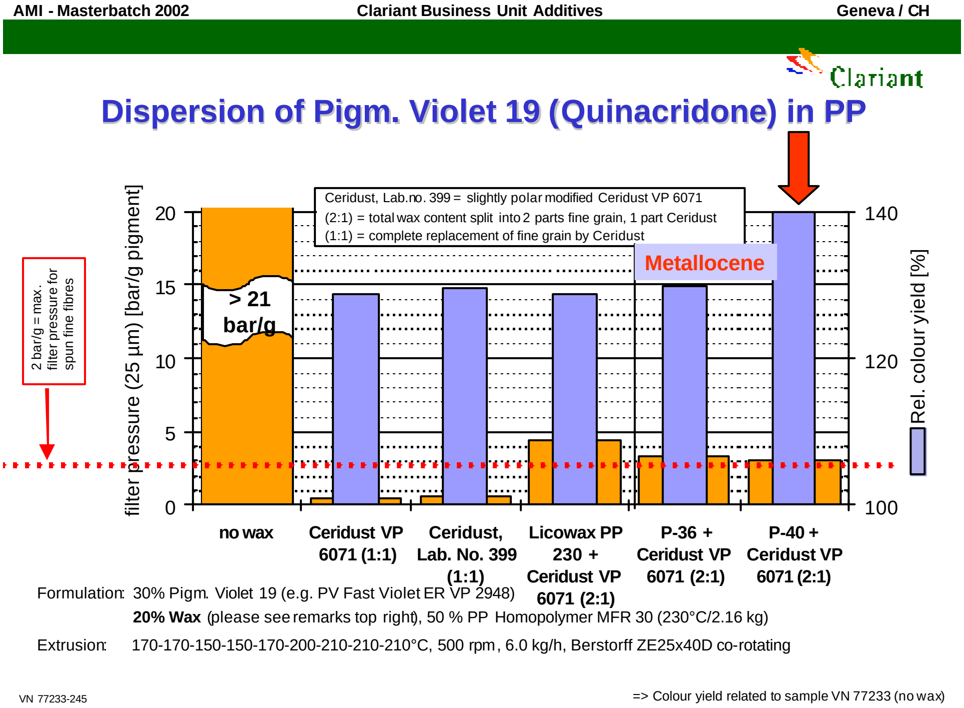
September 12, 2001

Dr. Zaeh / Dr. Hess
Clariant Business Unit Additives

VN 77090-099 + 77221

Fig. 4: Dispersion of Pigment Yellow 155 in Polypropylene

Pigment Yellow 155 is widely used in polypropylene carpet fibers applications , which makes the need to disperse it well even more urgent – specially if used in fine denier fibers. The examples above show an improved low filter value (yellow bar) and a fine high color yield (blue bar) for the combination of our new metallocene wax Licocene® PP 6100 in combination with the Ceridust version thereof. Remarkable here is the drop in filter value even compared to a „standard“ Ceridust combination.



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Dispersion of Pigm. Violet 19 (Quinacridone) in PP

Ceridust, Lab.no. 399 = slightly polar modified Ceridust VP 6071
(2:1) = total wax content split into 2 parts fine grain, 1 part Ceridust
(1:1) = complete replacement of fine grain by Ceridust

Formulation: 30% Pigm. Violet 19 (e.g. PV Fast Violet ER VP 2948)
20% Wax (please see remarks top right), 50 % PP Homopolymer MFR 30 (230°C/2.16 kg)

Extrusion: 170-170-150-150-170-200-210-210-210°C, 500 rpm, 6.0 kg/h, Berstorff ZE25x40D co-rotating

VN 77233-245

=> Colour yield related to sample VN 77233 (no wax)

Fig.5: Dispersion of Pigment Violet 19 into polypropylene

Pigment Violet 19 is , as probably all quinacridone pigments , being considered to be difficult to disperse into polymer matrices , specially no-polarity polyolefins with poor wetting capabilities because of their high viscosity and a challenging final application like fiber or film. When looking to the results , it is found , that filtervalues are best (lowest) when only using Ceridust – color strength is improving with the addition of a metallocene PP-copolymer (P-40) with excellent wetting capabilities , so this combination would be the primary choice for film applications.

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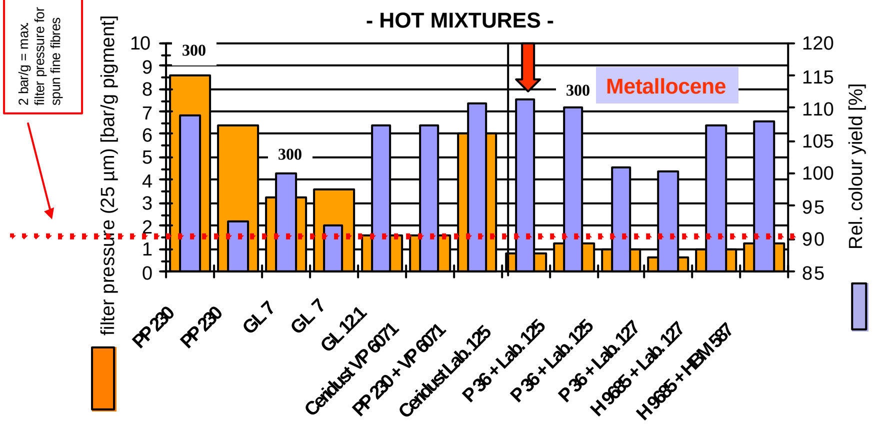
Dispersion of Pigm. Red 48:2 in Polypropylene



Formulation: 40% Pigm.Red 48:2 (e.g.Lithol Scharlach K 4461), 30% Wax, 30% PP Homopolymer MFR 30 (230°C/2.16 kg)

Extrusion: 180-200-190-170-150-170-190-180-175°C, 300 // 500 rpm, 5.0 kg/h, Berstorff ZE25x40D co-rotating

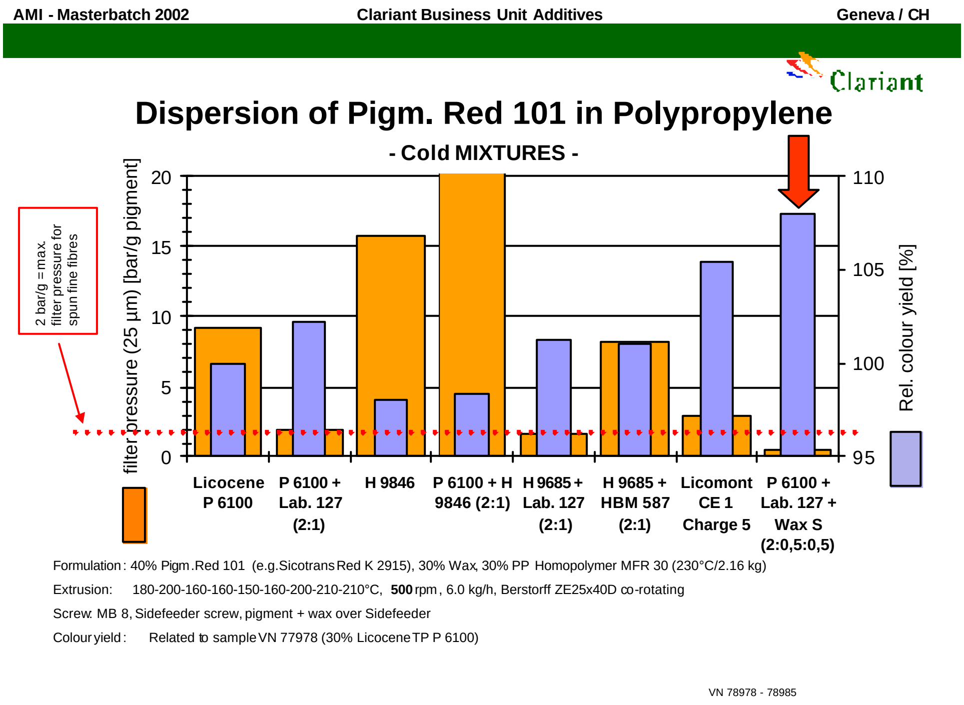
Colour yield: Related to sample VN 77948 (30% Gl 7, hot mixture)

VN 77947-77956 + 78227 + 77883 - 77884

Fig.6: Dispersion of Pigment 48:2 into polypropylene

Pigment 48:2 is not a typical pigment for use in plastics , it stems more from the toner area, where it is widely used. It's sensitivity to shear and consequent destruction using too much shear stress makes it a difficult challenge to disperse in polypropylene.

As the results show , specially our very fine ground metallocene Ceridust (particle size around 5 µm) is „embedding“ this pigment to an extent not to destroy but successfully disperse it. This effect , using highly crystalline isotactic **and** low molecular weight polypropylene waxes to achieve this „ball mill effect“ can only be realized with metallocene waxes.



Dispersion of Pigm. Red 101 in Polypropylene

Formulation: 40% Pigm.Red 101 (e.g.Sicotrans Red K 2915), 30% Wax, 30% PP Homopolymer MFR 30 (230°C/2.16 kg)

Extrusion: 180-200-160-160-150-160-200-210-210°C, **500** rpm, 6.0 kg/h, Berstorff ZE25x40D co-rotating

Screw: MB 8, Sidefeeder screw, pigment + wax over Sidefeeder

Colour yield: Related to sample VN 77978 (30% Licocene TP P 6100)

VN 78978 - 78985

Fig.7: Dispersion of Pigment Red 101 into polypropylene

Pigment Red 101 is a stable transparent (i.e. fine particle size) iron oxide pigment , so the only inorganic pigment within all the other examples of organic pigments we have looked at so far. Due to the relative fine particle size , it is comparably difficult to achieve good dispersion for challenging applications like thin film.
Looking for the results , we can state , that the use of –even functionalized- polypropylene waxes **including the metallocenes** alone does not get us to the top. There is some additional „dash“ of functionality needed – achieved as you can see by adding Licowax® S – a straight montan acid wax with very high functionality per chain length. The result is even more remarkable since filter value drops significantly even compared to a metallocene Ceridust combination.

To **summarize the part of pigment dispersion into polypropylene**:

- *With the new metallocene waxes (Licocene®) and their Ceridust form , there is significant improvement dispersing organic pigments like Pigment Yellow 155 or Pigment Red 48:2 into polypropylene.*
- *Since pigments and their functionality are different , there is also tailormade solutions available for every task , i.e. every combination of pigment and base resin.*

Another aspect is the influence of the processing stabiliser of the dispersion (**chart 3**). Including a pigment or a filler in a formulation increases the melt viscosity significantly (the filler as an example is more suitable because the effect is more pronounced compared to a pigment). Consequently the damage of the polymer due to higher shear forces increases, leading to reduced molecular mass of the polypropylene. This results in lower shear forces and with this in reduced dispersion of the filler. The addition of a standard antioxidant package reduces the effect already but still inhomogenities can be seen. Only by the addition of a suitable processing stabiliser it is possible to achieve a good and homogeneous dispersion and distribution of the filler. As a further consequence improved mechanical properties of the final article can be achieved (**chart 4**).

3 Direct impact of additives on the colour

Apart from products to increase the pigment dispersion a lot of additives to improve the properties of the final article were added. Their direct influence on the colour mainly results in a different colour yield or tone. One reason for this can be a direct interaction of the additive with the pigment.
Another possibility is the lubricating effect of some additives reducing shear forces in the melt. Depending on the additive a stabilising effect on the polymer can be observed, avoiding chain scission during processing. Both effects (lubrication and avoiding chain scission) result in different shear forces in the melt and as a consequence in a different dispersion and distribution of the pigment.

The improved pigment dispersion for Pigment Green 7 in PA 6 is shown in **chart 5**. The addition of a small amount of Nylostab S-EED via masterbatch results in a significantly higher colour yield in the carpet fibre. In **chart 6** the influence of different light stabilisers on PP during multiple extrusion is shown. It is quite obvious that there is a different impact of the light stabiliser on the polymer. This can explain the different colour strength of injection moulded PP plaques in dependence on the light stabiliser in **chart 7**. The same effect but with different pigments is shown in **chart 8**: The amount of pigment to achieve the same colour strength as without a light stabiliser is shown for two different light stabilisers. Depending on the pigment more or less pigment may be needed to achieve the same colour strength.

4 Long term effects during usage of the product

The long term effects leading to discolouration are mainly based on the impact of heat and/or of radiation, especially UV radiation. An pure thermal effect is the discolouration of phenolic antioxidants during service life time. This leads typically to a yellowish, orange or pink tint overlapping with the original colour of the product. This effect is well known and will not be discussed here.

A further reason can be the UV degradation of the polymer on the surface of the article, which results in the so called surface brittleness. The polymer chains degrade under the influence of the UV light forming small cracks on the surface. The cracks finally lead to a different reflection behaviour of the surface resulting in a changed colour - even though the pigment remains unchanged. **Chart 9** shows the changes in colour for yellow pigmented HDPE pipes during UV ageing depending on different UV stabilisers. It is inevitable that such an embrittlement has consequences for the mechanical properties of the pipes. These are shown in **chart 10** and it confirms what could be expected: the UV stabiliser that protects the surface better against the UV light maintains not only a better colour but the mechanical properties remain on a higher level as well.

Extractive media affecting the polymer is another long time effect which can cause discolouration. In **chart 11** the impact of hot water storage on the colour of blue pigmented HDPE is shown. The most significant increase in colour can be seen after storage with Hostanox O 10 as a phenolic antioxidant. The discolouration is much less pronounced if instead of this Hostanox O 3 is used as antioxidant. The individual property of different phenolic antioxidants to form coloured products under special conditions is quite obvious, without or in combination with light stabilisers.

The impact of the UV light on the pigment can be a further reason for discolouration. This effect depends without saying mainly on the chemical structure of the pigment, which determines its light stability. Often it is not obvious if the discolouration of a pigmented product origins from the brittle and crazy surface or if the pigment itself degraded under the influence of UV light.

In **chart 12** an example is shown were the pigment was destroyed under the influence of the UV light . The sample was cut after artificial weathering and the cross section of the HDPE plate is shown. In this case it was possible to protect the pigment by the addition of an UV absorber.

The surface of the plates was still in good shape after UV ageing. This indicated that the polymer was not damaged. Therefore it was interesting to have a look at the mechanical properties. In **chart 13** tensile impact strength of the samples was determined and no significant differences could be found, neither between these both, nor compared to the zero values.

Both observations, the picture with the bleached pigment and the mechanical properties, prove, that in this case only the pigment was destroyed by the UV light, but the polymer was still in good shape. The polymer was properly protected by a HALS (hindered amine light stabiliser), the pigment could in this case be protected by the further addition of a UV absorber.

This is in contrast to the above mentioned example of **char9 and 10**, where the UV light damaged the polymer, resulting in discolouration and loss of mechanical properties.

An example to improve light fastness of pigmented PA 6 fibres is shown in **chart 14**. The different discolouration of 5 pigments in fibres with or without Nylostab S-EED during 4 FAKRA cycles is quite obvious.

At this point the influence of pigments on the other properties of the final product should be mentioned at least with one example. The UV stability depends tremendously on the type of pigment used. It is well known that for outdoor plastics applications only special titanium dioxide grades should be used. If the wrong one is chosen the plastic will degrade unexpectedly fast. For organic pigments the situation is not that tremendous, but in **chart 15** it is clearly shown that the type of pigment clearly influences the UV stability of the fibres.

5 Conclusion:

Pigment dispersion is today quite well investigated and most impacts are known. This is the prerequisite to develop improved dispersing aids like the metallocene waxes. Knowing the interactions on the one hand and being able to produce tailor made waxes on the other hand offers the possibility to produce the most suitable waxes for the pigment dispersion. Metallocene waxes are our contribution for improved pigment masterbatches.

The impact of all the other additives used in plastics onto the colour is somewhat less clear. Some single effects are well investigated, but we are still far away to have a clear picture about all the interactions that can occur. Here the situation is comparable with a puzzle, where we have already put together some parts from here and there, but it is still a long way to the whole picture. Before reaching this point it is inevitable to use the experience of well skilled specialists in order to minimise risks and costs. If possible the targeted working environment for the final pigmented article should be included into the development testing program.

chart

Clariant

Exactly your chemistry

http://www.additives.clariant.com

Improved pigment dispersion with waxes

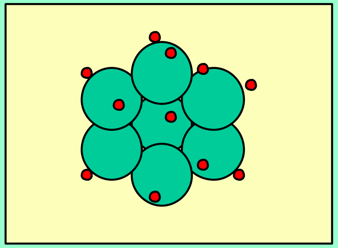
Various pigments in polypropylene

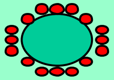
Clariant

Improved Pigment Dispersion

Processing Steps

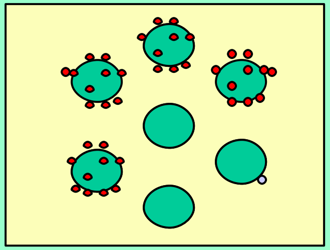
Pigment Wetting (dispersing agent)



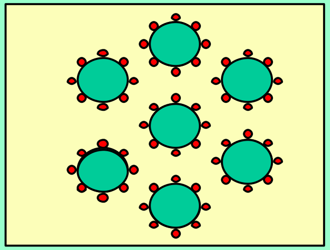


surplus of dispersing agent
(e.g. wax) is beneficial

Dispersion



Stabilization



Dispersing agent‘s main features

- ⇨ **Drop point**
- ⇨ **Viscosity**
- ⇨ **Polarity**

- ⇨ **Viscosity**
- ⇨ **Thermal and Colour Stability**

- ⇨ **Polarity**
- ⇨ **Compatibility**
- ⇨ **Viscosity**

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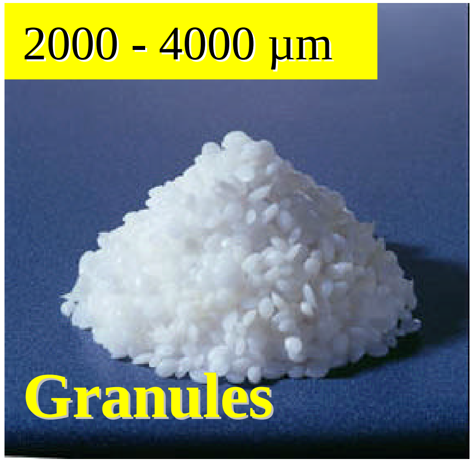
Clariant: Supply Forms for Waxes


2000 - 4000 µm

Granules

Licomont

Licolub

Licowax

Ceridust

Registered trademarks


< 2000 µm

Fine grain


Powder

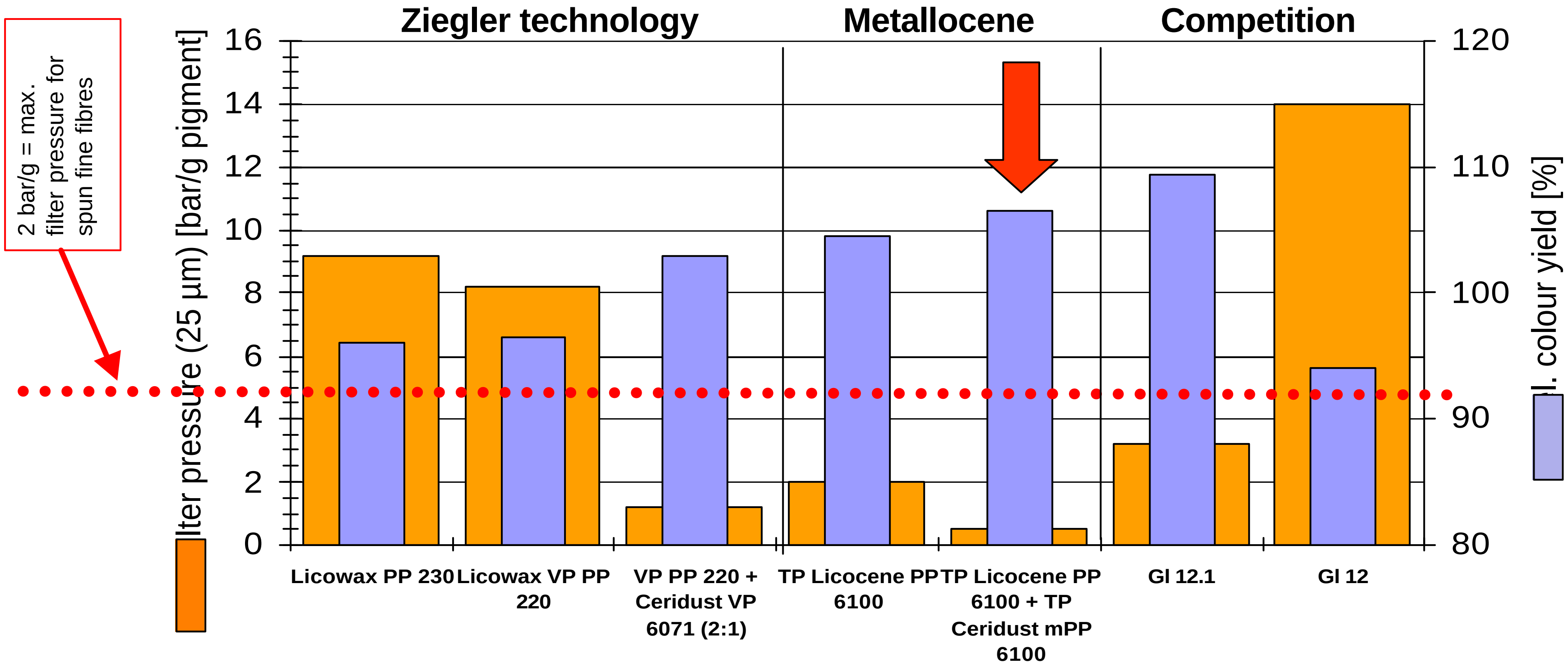
< 500 µm


Ceridust®

~ 10 µm

Dispersion of Pigm. Yellow 155 in Polypropylene

- HOT MIXTURES -

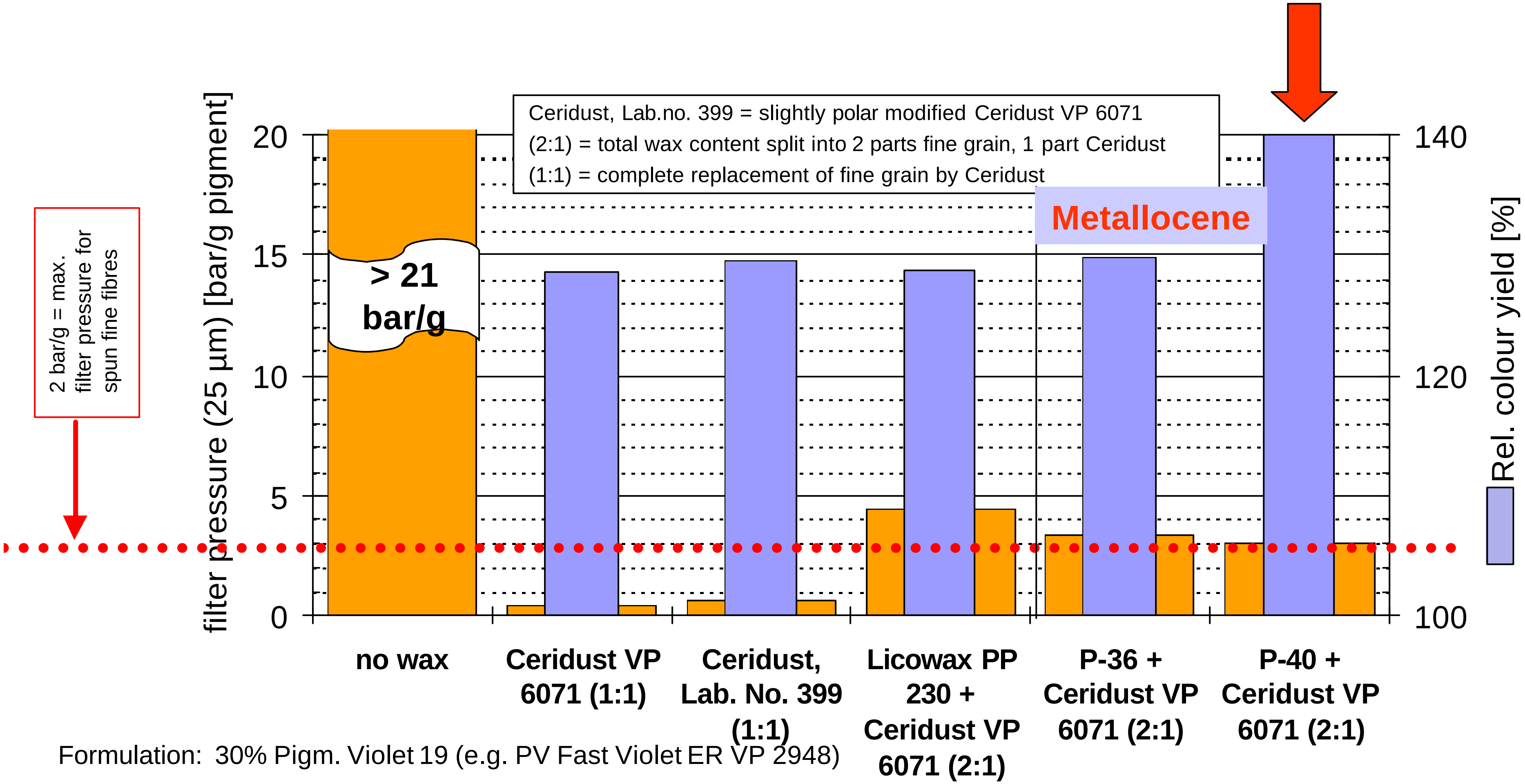


Formulation: 40% Pigm. Yellow 155 (e.g. Graphtol Yellow 155), 30% Wax, 30% PP Homopolymer MFR 30 (230°C/2.16 kg)

Extrusion: 190-170-150-150-170-200-210-210-190°C, 50 rpm, 6.0 kg/h, Berstorff ZE25x40D co-rotating

Colour yield: Related to sample VN 77100 (30% PP 230, cold mixture)

Dispersion of Pigm. Violet 19 (Quinacridone) in PP



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20% Wax (please see remarks top right), 50 % PP Homopolymer MFR 30 (230°C/2.16 kg)

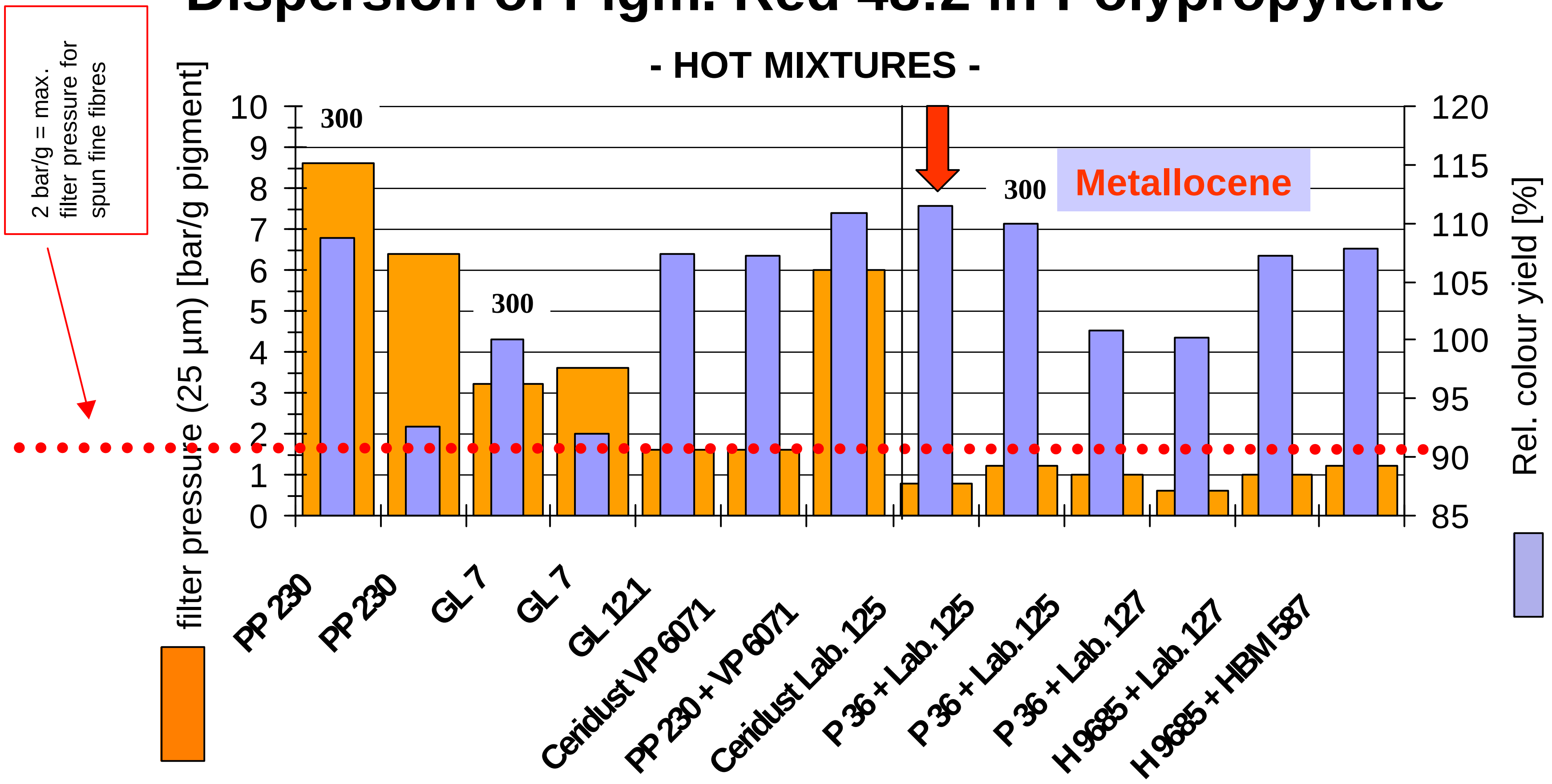
Extrusion: 170-170-150-150-170-200-210-210-210°C, 500 rpm, 6.0 kg/h, Berstorff ZE25x40D co-rotating

VN 77233-245

=> Colour yield related to sample VN 77233 (no wax)

Dispersion of Pigm. Red 48:2 in Polypropylene

- HOT MIXTURES -



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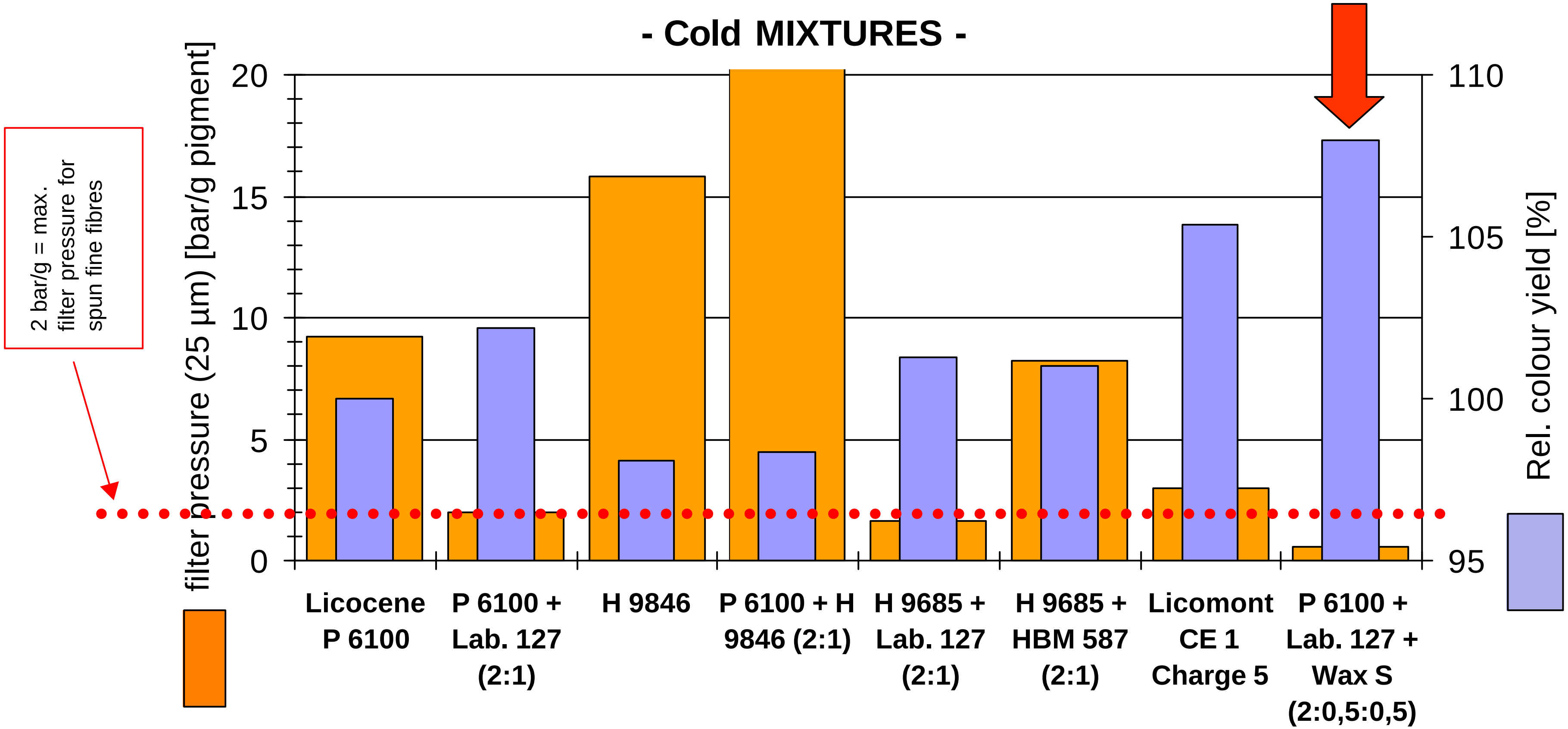
Extrusion: 180-200-190-170-150-170-190-180-175°C, 300 // 500 rpm, 5.0 kg/h, Berstorff ZE25x40D co-rotating

Colour yield: Related to sample VN 77948 (30% Gl 7, hot mixture)

VN 77947-77956 + 78227 + 77883 - 77884

Dispersion of Pigm. Red 101 in Polypropylene

- Cold MIXTURES -



Formulation: 40% Pigm.Red 101 (e.g.Sicotrans Red K 2915), 30% Wax, 30% PP Homopolymer MFR 30 (230°C/2.16 kg)

Extrusion: 180-200-160-160-150-160-200-210-210°C, **500** rpm, 6.0 kg/h, Berstorff ZE25x40D co-rotating

Screw: MB 8, Sidefeeder screw, pigment + wax over Sidefeeder

Colour yield: Related to sample VN 77978 (30% Licocene TP P 6100)

Improved Dispersion in Polypropylene

Best choice for High Quality Masterbatches
for demanding applications in Polypropylene are

- ⇨ **Polymerized Polypropylene Waxes**
  (powder grades)
- ⇨ **Mikronized Polypropylene Waxes**
  (®Ceridust = Tradename of Clariant)
- ⇨ **New improved option: Metallocene Polypropylene Waxes**

Pigments are different → **Dispersing additives have to be different as well**