Powder Coatings – A New Finishing System for Leather Industry

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ABSTRACT

After many years of our research work, powder coating can now be firmly established as a feasible new finishing system for leather finishing. Powder coating is a solid coating formulation in the form of dry, free flowing and fine powders at room temperature. It has the distinct advantages of using no solvents and the powders being 100% reclaimable. Other advantages include no need for extensive and overlapping spraying. Powder coatings are therefore an economic, energy-efficient, and ecological technology. Despite powder coatings’ many advantages, they are not applicable for leather finishing mainly for two reasons. Firstly baking or curing temperatures of current powder coatings are too high for heat-sensitive substrates such as leather and secondly, current powder coatings are limited to amorphous polymers of high glass transition temperature for technical reasons and are inherently hard, not flexible. We have, however, broken the mould of current powder coating technology and developed a polyurethane-based powder coating resin, suitable for powder coating formulation. Such powder coatings can be cured at temperature below 100°C and give a highly flexible and tough coating suitable for leather finishing. The technology also includes a high-speed “dry roller coat” capable of producing a coating as thin as 10 µm.

INTRODUCTION

A powder coating is a solid coating formulation in the form of dry, free flowing and fine powders at room temperature. Each particle contains all ingredients in the formulation, well mixed with minor components such as colorants, flow agents and crosslinkers etc., in a matrix of the major film-forming component polymer (binder). The powder is applied to the substrate surface and fused to form a continuous film at elevated temperatures which are often referred to as baking or stoving temperature. The baking temperature is typically in the range of 160 – 200°C for thermal curing formulations.

The distinct advantages of powder coatings over conventional liquid systems are:

1. Reclaiming powders during application is possible that leads to almost 100% utilization of the coating materials
2. No emission of volatile organic compounds (VOCs)
3. An even coat can be achieved with one spray, without the need for extensive and overlapping spraying
4. Cost per unit area is cheaper than conventional methods
Powder coatings are therefore an economic, energy-efficient, and ecological or environmentally friendly surface coating technology. They are also clean and convenient to use, since they are in dry solid form.

Despite powder coatings’ many advantages, they are typically used for coating metals and are generally not employed in coating heat-sensitive substrates such as leather, wood and plastics, which demand lower baking and/or curing temperatures preferably below 120°C. However, lower curing temperatures are not possible with traditional thermal curable powders. This is because reactive crosslinking agents for low curing temperatures will adversely affect the shelf-life of powders, and adversely affect the flow due to viscosity increasing too fast during the baking and curing process. The ultimate solution to this problem may lie in the use of low temperature ultraviolet (UV) radiation curable powder coatings, because UV curing separates the flow-out step from the curing or crosslinking step. Furthermore, UV curing is very fast (in the order of seconds), there is no need for prolonged heating for complete cure.

Current powder coatings, based on amorphous polymers as the base resin, also suffer from two drawbacks. The first is that the film formed is inherently hard, not flexible, because a high T_g polymer (usually above 50°C) is required to give the powder the properties of resistance to blocking (giving a free flowing fine powder) during storage at room temperature. The second is poor flow properties. Crystalline polymers may be incorporated with amorphous polymer in the formulation of UV-curable powder coatings, chiefly to improve the flow properties of the formulations. But the incorporation of crystalline polymers does not help resolve the problem of inflexible film.

This paper is related to low baking temperature UV-curable powder coating resins for highly flexible and heat-sensitive substrates such as leather, but which are nevertheless hard solid powders stable on storage. Such resins and compositions are based on crystalline or semi-crystalline polymers but when subject to melting and flow-out at low temperatures (60°C – 120°C) and upon curing in molten state by UV, will give a highly flexible coating having either complete amorphous, non-crystalline, low glass transition temperature (T_g) polymeric matrix or low degree of crystallinity, low T_g polymeric matrix.

**CONCEPT AND EXPERIMENTATION**

Before applying to substrate and baking, a powder coating must be “hard” fine solid powders which will not fuse when stored at room temperature. This is usually achieved by using amorphous polymers of high T_g (above 50°C). After baking and curing, such polymers will inevitably give a rigid film because of their high T_g values. Therefore the coating tends to be rigid and inflexible. The use of high T_g polymers also require higher baking temperature to achieve sufficient flow. The consent minimum temperature is around 120°C for sufficient flow based on amorphous polymer. For good flow properties at low temperatures, a crystalline polymer is highly desirable, because its viscosity decreases much more rapidly than amorphous polymer as the temperature increases above the melting point. However, crystalline polymer will also result in rigid film. Therefore current powder coatings do not provide a coating film suitable for leather finishing.
To break the current mould of powder coating, we proposed to use crystalline or semi-crystalline polymers as the base resins for powder coatings to achieve the dual purpose of storage stability and film flexibility. These semi-crystalline polymers have carefully designed and fine-tuned molecular architectures and structures that can be converted to non-crystalline, low $T_g$ polymer film upon further chemical reactions during the baking and curing step. Low $T_g$ polymer can be used because that “hard” solid property is provided by crystallinity rather than chain rigidity (i.e. high $T_g$). Theoretically it is possible to achieve the conversion from crystalline to non-crystalline polymers, or at least low crystallinity, by disrupting the structural or stereo-regularity of polymer chain that makes the polymer crystalline. Random copolymerisation of different crystalline units, introducing chain branching and crosslinking etc are all available common methodologies that can be utililzed to disrupt structural or stereo-regularity of polymer chain.

A polyurethane-based, UV-curable resin system was eventually chosen after experimentation and considerations of issues such as low cost and simplicity of the chemistry involved. For low temperature application, UV-curable functional groups were incorporated but thermally curable functional groups can also be used in principle. Variables in our experimentation include molecular weight of resins, type of crystalline structure, type and content of branches, and type and content of crosslinking points, etc.

To achieve a thin coating, we also tested the Electromagnetic Brush (EMB) technology developed by DSM Resins.

RESULTS

Figure 1 shows the DSC curves for a polyurethane resin, before and after curing. This resin belongs to a polyurethane resin system or series that we denoted PUA. It is clear that before curing, this resin polymer has a melting transition around 60°C; after curing there is no melting transition detected but a glass transition temperature at -20°C. Thus it is evident that the curing process has converted the crystalline polyurethane to a non-crystalline, amorphous and low $T_g$ polymer that give a flexible film. $T_g$ values after curing fall in the range of –5 to -25°C for this PUA series.

A leather sample coated with this PUA is shown in Figure 2. In the formulation of the coating, 1.5% (w/w) Irgacure 184, a photo-initiator for UV curing, was added. The coating formulation was applied to leather and heated to 85-90°C and cured by UV radiation at an intensity of about 1 J/cm² for 20 seconds. The flexibility of the coating is evident when the leather sample is bent in the fashion as shown in Figure 2 and there is no crack on the coating.
Figure 1. DSC curves of a PUA resin. The bottom curve is before curing and the top curve is after curing.

Figure 2. A leather sample finished with a UV-curable powder coating based on PUA series.
It was found that there exists a window of optimal compositions of the PUA resins for storage stability and reduction of crystallinity, depending on the branching content and crosslinking density, as shown in Figures 3 and 4. Clearly a complete non-crystalline film requires a composition within the boundary of this window.

**Figure 3** The effect of crosslinking density on the crystallinity of PUA series before (□) and after (■) UV-curing.

**Figure 4** The effect of crosslinking density on the melting point of the PUA series before (□) and after (■) UV-curing.
It was also discovered that the Electromagnetic Brush (EMB) technology developed by DSM Resins is the best technology for applying powders to leather substrates. The principle of EMB is similar to photocopying, and a modified EMB (see Figure 5) incorporating a transfer drum is applicable to dry leather that is not electrically conductive. EMB is a “dry roller coat” technology that has the following advantages:

- High Speed
- Adjustable thickness
- No powder overspray
- No recycling needed

Figure 6 shows the cross-section of a leather sample coated with powder coating using EMB. The thickness of the coating is about 10 μm, close to the thickness of topcoat in leather finishing; whereas the conventional electrostatic spraying technology would typically give a film thickness of 70 μm.

**Figure 5.** A laboratory EMB with transfer drum (reproduced with permission of DSM Resins).
CONCLUSION

A ground-breaking new powder coating resin system has been developed that is suitable for coating highly flexible and heat-sensitive substrates such as leather. It provides a new economic and ecological surface finishing technology for the leather industry.