



HOLLIDAY PIGMENTS

White Paper

January 2010

Ultramarine: The Eternal Pigment

When the ancient Egyptians came to decorate the works of art that they buried with their Pharaohs, they used a blue pigment of such brilliance that it would enhance the quality and value of any object. The pigment was derived from the semi precious mineral, Lapis Lazuli, and it continued to be used for many centuries.

The quality of the blue produced by this method was never in question. But the scarce availability and difficulty of extracting the pigment meant that the cost was high and the pigment could only be used in the most prestigious applications. It was clear that a rich prize awaited anyone who could devise a synthetic route to manufacture this pigment, which is now known as Ultramarine Blue.

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Discovery of the Synthetic Process

The process for the synthetic manufacture of Ultramarine was discovered in 1828 by a French scientist, Guimet. Soon there were factories springing up all over Europe as the more affordable synthetic pigment stimulated the use of Ultramarine in many applications.

Of particular note was the discovery that a small amount of Ultramarine would, if added to the rinse water during the laundering process, absorb the unwanted yellow undertone which became apparent as white clothing aged. This unwanted yellow caste was replaced by a blue undertone that suggested extra brightness and cleanliness. In fact it was for this purpose in 1884 that James Reckitt built an Ultramarine factory in Hull to extend his range of existing laundry products. This factory was still producing Ultramarine under the name of Holliday Pigments Limited up until 2007 and today the company remains a world leading supplier of Ultramarine Blue.

Modern Applications

While Ultramarine continued to be used both in artists' colours and laundry products, it was the birth of the plastics industry which stimulated the development of the Ultramarine pigment that we know today. Ultramarine had been perfect for use in artists' colours due to its unique shade with unrivalled brightness and its excellent lightfastness. It was non-toxic and non-irritant, ideal for an application like laundry with its inevitable skin contact. But add to these virtues its excellent heat stability, an obvious advantage in a high temperature application such as plastics, and it is no wonder that Ultramarine soon became regarded as an indispensable plastics colourant.

But how does Ultramarine come to possess such a combination of admirable properties?

The answer is in its production process – which is itself a fascinating story.

The chromophore responsible for the blue colour in Ultramarine is based on sulphur and has the formula S_3^{2-} . It is strange to think of a yellow chemical like sulphur giving a blue colour, but in this particular form it does.

However, the discovery of the chromophore was only one step in the development of a synthetic process to manufacture Ultramarine. The problem is that the chromophore is unstable and is readily oxidised to non-pigmentary sulphate.

Kiln Reaction

The chromophore, therefore, needs to be protected from these chemical reactions and this is achieved by stabilising it within the protective cage structure of a clay (kaolin) lattice.

The production process involves heating a mixture of sulphur, clay and sodium carbonate to a temperature of almost 800°C in a kiln, excluding air to prevent premature oxidation of the sulphur before the reaction temperature is reached. After sufficient residence time at this peak temperature to form the initial chromophore, the mixture is allowed to cool before air is slowly allowed into the kiln to complete the reaction with an oxidation stage. This high temperature process takes more than two weeks to complete.

With this knowledge of the production process we can already see the reason for some of the desirable qualities of Ultramarine. The chromophore is very unusual, leading to a unique shade which cannot be matched by other pigments. Being transparent, Ultramarine adds an attractive blue undertone to transparent polymers as well as neutralising unwanted yellowness in opaque white plastics. The high temperature manufacturing process provides the Ultramarine pigment with an inbuilt stability to heat. In fact, Ultramarine blue pigments are stable to more than 350°C, high enough for use in all common plastics. Finally, the raw materials are all quite benign - no heavy metals are used in the production of Ultramarine and organic compounds would not survive the high manufacturing temperature. Ultramarine is one of the safest known pigments by virtue of its raw materials and production process.

Removing Impurities

This high temperature process produces the 'raw' Ultramarine, but the process is far from complete. After this 'dry' process it is necessary to refine the raw Ultramarine, a process which starts by slurring the raw Ultramarine with water. This second stage is commonly called the 'wet' process. In this stage the impurities present within the raw Ultramarine are removed. The most important of these is unreacted sulphur, which would otherwise give rise to an odour when used in high temperature applications like plastics. Soluble material, primarily sodium sulphate, is also removed.

Finally the pure Ultramarine pigment is ground to its final particle size then separated from the water. The grinding process leaves a broad spread of particle sizes with a range from less than 1 up



to 3 microns. By a process known as classification, these particles are separated into a number of discrete fractions. Each fraction is dried to produce a fine powder.

Why is a fine particle size so important?

The properties of an Ultramarine pigment depend primarily on its particle size.

Finer particles are stronger in tinting power, they are brighter and also greener in undertone than the coarser particles produced at the same time. Ultramarines intended for technical applications range from less than 1 to 3 microns, Ultramarines coarser than this are normally confined to low quality applications such as laundry powders (see Figure 1). The correct product can be selected from the particle size range available based on tint strength, undertone and brightness.

Once again knowledge of the Ultramarine manufacturing process provides another indication of the final property of the Ultramarine. Pigment particles of 1 to 3 microns are relatively large and as one might expect, Ultramarine disperses very easily.

Benefits of Ultramarine

So, amongst its advantages, Ultramarine has:

- A unique shade of unrivalled brilliance
- Excellent lightfastness
- Excellent heat stability
- Worldwide safety approvals for use in food contact plastics and toys
- The capability to improve the undertone of off-white articles

In addition, Ultramarine has no adverse effect on the dimensional stability of polyolefins, which is important in large or complex polyolefin mouldings. This is because Ultramarine is an inorganic pigment. Organic pigments almost always have an adverse effect on the dimensional stability of polyolefin mouldings.

Acid Resistance

Ultramarine has many positive attributes which make it ideal for most plastics applications, but there are some potential problems to be aware of.

In its standard form, Ultramarine is sensitive to acids. Even mild acids will attack the chromophore and destroy the colour. However, Holliday Pigments has developed acid resisting grades for such applications. In these grades the pigment particles are protected by a coating. By selection of the correct grade, Ultramarine can still be used in polymers such as PVC, which may have acid degradation properties, or in containers for acidic products like fruit juice. Acid resisting grades are also recommended for outdoor applications which may be exposed to the effects of acid rain.

Summary

Ultramarine has been the blue pigment of choice for thousands of years. Despite more choice in the blue area of the spectrum the properties which made Ultramarine popular so long ago are still valued just as much today. And probably thousands of years in the future our descendants will still be marvelling at the brilliant colour of Ultramarine, the eternal pigment.

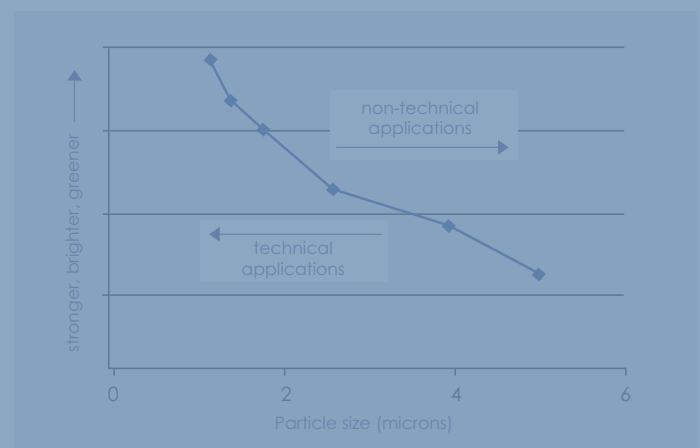


Figure 1:- How particle size impacts on application.



About Holliday Pigments

Holliday Pigments is a world leading supplier of Ultramarine pigments, which are used in a variety of applications including plastics, coatings, cosmetics, artists' colours and printing inks. Exporting to over 80 countries, Holliday Pigments has dedicated customer and technical service teams at its factory in France and its commercial office in Singapore.

Holliday Pigments has a proud 125-year history in the manufacture of technical quality Ultramarine and is the only Ultramarine manufacturer in the world to have invested in Flue Gas Desulphurisation technology, reducing sulphur dioxide emissions inherent in the manufacturing process by more than 99.5%.

In August 2008, Holliday Pigments joined Rockwood Holdings Inc., becoming an important addition to the Color Pigments and Services Division. Rockwood's Color Pigments & Services Division is one of the largest worldwide suppliers of colored pigments for construction, coatings, plastics and specialty applications.

The Division's manufacturing sites and customer service centres are located in the United States, United Kingdom, Italy, Germany, Australia and China with additional sales offices located in Singapore.

The Rockwood Color Pigments & Services Division is part of Rockwood Holdings Inc., Princeton, N.J., U.S.A. Rockwood Holdings, Inc. is a leading global specialty chemicals and advanced materials company. Rockwood has a worldwide employee base of more than 9,500 people and annual net sales of approximately \$3.1 billion. The company focuses on global niche segments of the specialty chemicals, pigments and additives and advanced materials markets.

For more information on Rockwood, please visit www.rockwoodpigments.com

Further information on all Holliday Pigments' products is available from:

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