



HOLLIDAY PIGMENTS

White Paper

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Ground-Breaking New Acid Resistant Ultramarine Blue Pigment Demonstrates all Round Superiority

Ultramarine blue is one of the world's most tried and trusted pigments for premium applications in plastics, cosmetics, food packaging, artists' colours and paint. A pigment with a unique and vibrant red-blue shade, it cannot be recreated by other pigments, and is still basically manufactured according to the principles of Jean-Baptiste Guimet's original process, discovered in 1828.

However, in over 125 years of manufacturing ultramarine blue, Holliday Pigments has never stopped refining its production process, to develop products which are best suited to specific applications. In fact, in its position as a leading manufacturer of ultramarine blue, Holliday Pigments has pioneered many of the market leading grades available today in, for example, plastics and automotive paint.

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Defying acid

Holliday Pigments has recently made a major advance with a solution to the problem of maintaining pigment hue and intensity in acid conditions. While previously available acid resistant grades from Holliday Pigments had provided a good response to many of the difficulties posed under acid conditions, there were several specific parameters which needed further development.

Dissatisfied with the status quo on acid resistance, Holliday Pigments invested in fundamental research on the problem, which resulted in the launch of its Premier XAR grade. This valuable addition has already facilitated major orders in, for example, plastics for stadium seating at the Beijing Olympics as well as intense interest from many other users in Asia and in Europe.

Improvements on all sides

The new Premier XAR grade delivers dramatically improved resistance to acid degradation and also superior abrasion and weathering characteristics.

Given this step change in performance, it is worth looking at how the known acid sensitivity of ultramarine blue has been overcome to such an extent that it exhibits superior performance to previously available ultramarines.

The classic formulation of ultramarine blue is $\text{Na}_6(\text{Al}_6\text{Si}_6\text{O}_{24})\cdot 2\text{NaS}_3$, and it has a molecular structure which can be depicted by sodium and sulphur ions encapsulated in a β cage of sodium aluminium silicate (See fig. 1). The sulphur ions are vulnerable to reduction by free hydrogen ions, which quickly affect the colour.

Conventional acid resistance treatments have previously resulted in irregular coating thickness which limits acid resistance and increases sensitivity to abrasion.

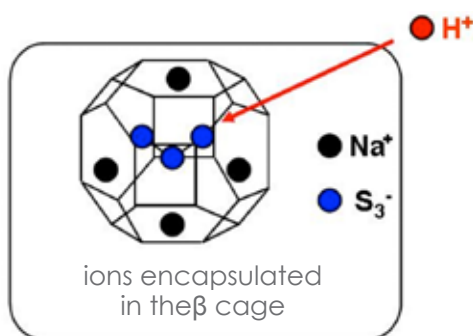


Figure 1:- Traditional Ultramarine Blue particle $\text{Na}_6(\text{Al}_6\text{Si}_6\text{O}_{24})\cdot 2\text{NaS}_3$ formula is easily attacked by acid.

Particle coating success

The new particle coating process for the XAR grade has resulted in all round superiority for the new product. Because of the importance of a high performing acid resistant grade within the market place, and the very significant improvement achieved by Holliday Pigments, its Premier XAR was subjected to a very severe battery of tests.

Standard acid resistance tests use both 10% (volume) hydrochloric acid (boil 1 hour, filter, wash and dry pigment, visual comparison versus colour standards) and 5N sulphuric acid (bubble 1 hour at 20°C, filter wash and dry, compare the tinting strength of a 1:5 reduction using a colour spectrophotometer).

Holliday Pigments' Premier XAR exceeded the performance of conventional grades in these tests. In more extreme tests, after boiling for up to 4 hours in 10% HCl, against a standardised acid resistance index of 10, XAR demonstrated a constant score of 9 while ordinary treated acid grades deteriorated in more or less a straight line relationship with elapsed time to score 6 after 4 hours.

Resistance when formulated in plastic confirmed this dramatic improvement. Incorporated into plastic plaques, and half immersed in 20% HCl for 72 hours, Premier XAR showed 20% fading compared to the 70% fading of standard treated grades. (Fig 2)



Figure 2:- Incorporated into plastic plaques, and half immersed in 20% HCl for 72 hours, Holliday Pigments' Premier XAR (right) showed 20% fading compared to the 70% fading of standard treated grades.

Resistant coating

Abrasion resistance is important when dispersing Ultramarine in a wide range of applications. Abrasion of the protective coating during dispersion can cause significant initial colour loss when exposed to acids even if the pigment itself is otherwise resistant. The test mixed 1g of the ultramarine pigment with 50g water and 10g of glass beads with a diameter of 1.5mm. The solution was shaken for 20 minutes, and then subjected to the H₂SO₄ acid test, as discussed previously.

When compared with the results obtained with unabraded pigment, the previous best acid resistant ultramarine blue lost 13% of its colour strength while Premier XAR lost half of that, only 7%. The subjective viewpoint is that the previous grades demonstrated noticeable pigment loss, while the difference with XAR was barely discernible – a testament to the more consistent coating thickness obtained.

Weathering front

The final area where the new acid resistant grade demonstrated its superior performance was in the highly important one of weathering. Many applications for which the brilliance of ultramarine blue is desirable are in constant exposure to weather and atmosphere; car paint work and stadium seating are just two examples. Acid rain poses a specific problem, especially in some industrialised areas of the world where technology to limit acid-forming emissions to the atmosphere are not in place.

The accelerated test comprised black panels, over coated with a carrier system formulated with Premier XAR, standard ultramarine blue, titanium dioxide or phthalocyanine. The tests included irradiance at 340nm with a power of 0.55W/m², held at a relative humidity of 40% and subjected to a cycle of 18 minutes wet (water spray) and 102 minutes dry. The rate of colour intensity change was measured over an exposure time of 15 days.

Previous weathering studies had been conducted in locations such as Florida and the UK (exposure over two years) and accelerated tests under accentuated UV levels over 2,000 hours. These had demonstrated that Premier XAR was markedly superior in stability to standard ultramarine pigments.

Gold medal applications

Within three months of its introduction in SE Asia at the end of 2007, and working closely with Holliday Pigments' then Hong Kong-based agent, orders were won for seats for an Olympic stadium with interest from a similar project.

Further application possibilities in plastics include PVC processing, chemical pipework - where retaining a strong blue colour as a visual signal may be important - and any exterior application where acid rain is encountered.

Holliday Pigments' Premier XAR is specifically recommended for optimum resistance to acid attack when used in plastics. For optimum resistance in other applications, a similar performance can be expected from Holliday Pigments' general purpose grade Ultramarine 59.



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' colors and printing inks. Exporting to over 80 countries, Holliday Pigments has dedicated customer and technical service teams at its factory in France.

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 centers are located in the United States, United Kingdom, France, Italy, Germany, Australia and China with an additional sales office located in Hong Kong. For more information on Rockwood, please visit www.rockwoodpigments.com.

The Rockwood Color Pigments & Services Division is a business unit 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 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.rocksp.com.

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

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