



HUBER ENGINEERED MATERIALS

Effect of Iron Content in Ground Calcium Carbonates on Accelerated Weathering Properties of Rigid PVC Pipe Compounds

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ABSTRACT

Ground Calcium Carbonate (GCC) is a natural mined material composed predominately of a relatively soft mineral known as calcite. However as a natural material, all ground calcium carbonate contains small amounts of other minerals as well as trace amounts of metal salts and oxides. Iron oxides and sulfides, in particular, are found in all deposits at levels which vary by the deposit. As iron is a known degradation catalyst for PVC, a survey of deposits, their iron levels, and effects on PVC pipe compound weatherability were studied and its effects quantified.

INTRODUCTION

It is well known that dehydrochlorination of PVC proceeds rapidly in the presence of Lewis acids such as FeCl_3 , ZnCl_2 , AlCl_3 , SnCl_4 , as well as several less common salts^(1,2). The role of iron as an impurity in PVC has been studied extensively⁽¹⁻⁹⁾. Early studies attributed its source to being due to abrasion of machinery parts. Later studies focused on the role of iron oxide containing pigments on stability⁽¹⁰⁾. Iron chloride has been shown to promote the dehydrochlorination of PVC, even in small concentrations⁽³⁻⁵⁾. Iron (II or III) oxide can react with hydrochloric acid (HCl), evolving from the dehydrochlorination reaction inherent in the high temperatures and shear encountered when processing PVC, particularly rigid PVC.⁽⁷⁾ Not only does this lead to the discoloration of the PVC, but in some cases can impact the properties of the PVC product.

Ground Calcium Carbonate (GCC) is a natural, not a synthetic material. The characteristics of a GCC are primarily a function of its median particle size, particle size distribution and its impurities. Impurities can take the form of other minerals, metal salts, and metal oxides. The role of impurities is of special concern.

Calcium-magnesium carbonate ($\text{CaMg}(\text{CO}_3)_2$) and silica are the most common mineral impurities in calcium carbonate⁽¹¹⁾. There is usually a small amount of magnesium carbonate (dolomite) associated with any calcite deposit. Other common impurities such as mica or graphite are sometimes encountered in small concentrations. None of these minerals pose any substantial effect on the processing of PVC at concentrations typical in commercial offerings suitable for PVC compounding.

Of greater concern is the concentration of iron (as iron oxide or sulfide) in the deposit. Iron levels in different deposits can vary greatly. Iron oxides and sulfides in GCC are particularly of concern because of their distribution. Since GCCs for rigid PVC applications are typically milled to between a 1-3 μm median particle size, the resulting surface area is on the order of 3- 10 m^2/g ! Obviously even small loadings of GCC can result in a significant amount of iron-containing surface area to be exposed for reaction. In addition to the dehydrochlorination during PVC processing, exposure to UV light can also result in discoloration of PVC. This study is aimed at understanding the impact that iron impurities in GCC can have on the weatherability of PVC.

EXPERIMENTAL

PVC Pipe Formulations – While most weatherability studies have focused on high loadings of TiO_2 in the formulations, the weathering of PVC pipe can also be of concern. PVC pipe is typically stored outside after extrusion with subsequent exposure to UV radiation. The generic NSF Standard 14 range formulation allows from 0.5 to 3.0 phr of TiO_2 to be used. As TiO_2 is one of the most expensive raw materials, PVC pipe producers try to minimize its use.

As a result, PVC pipe exposed to prolonged UV radiation may suffer “sunburn”, where the exposed surface discolors to an orange/brownish shade while the “underside” retains its original white color. While the physical properties are likely unaffected, it can result in product quality claims from the retail end users due to perceived poor quality of color appearance. This effect is especially pronounced during the Northern Hemisphere summer season and in southern latitudes where UV radiation is most severe.

Various nominal 3 μm median GCC products were obtained from producing locations in the USA. All products were produced from ore mined in that state’s geographic region with the exception of Hubercarb® W3N and VertiCal® 3T GCC products which are from ore of Caribbean origin milled in Quincy, IL by Huber Carbonates, LLC. Two surface treated products were included for comparison, Hubercarb G3T produced by Huber Carbonates, LLC at Marble Hill, GA to compare to untreated Hubercarb G3, and VertiCal 3T product as an analog in median particle size to W3N, albeit with a much lower Specific Surface Area (SSA).

The products were measured for the amount of iron by inductively coupled plasma emission spectrometry, EPA Method 6010B. Most of the products exhibited a moderate amount of iron in the 400 to 800 ppm range. The notable exception was the Caribbean ore with much lower average levels. Table 1 gives the iron results for these products.

Table 2 gives the PVC dryblend pipe formulation which holds the CaCO_3 constant at 5 phr, while examining TiO_2 levels of 0.5, 1, 1.5, 2 and 3 phr. Drop temperature was 220° F.

Table 1- Fe Levels for PVC Pipe Study

Location	Fe (ppm)
Caribbean (Hubercarb [®] W3N)	20
Caribbean (VertiCal [®] 3T)	81
Vermont	530
Alabama	520
Massachusetts	200
Texas (Hubercarb M3)	380
Illinois (Hubercarb Q3)	550
Georgia (Hubercarb G3)	740
Georgia (Hubercarb G3T)	1000

Table 2- PVC Pipe Formula

Ingredient	Manufacturer	PHR
PVC Resin 1091	Axiall Corp	100.00
Advastab [®] TM-694 Tin Stabilizer	PMC Organometallic	0.30
Calcium Stearate 10B	ACME Hardesty Co.	0.80
RL165 Paraffin Wax	Honeywell International	1.20
AC-629A Oxidized Polyethylene Wax	Honeywell International	0.15
Ti-Pure [®] R- 101 TiO ₂	DuPont	Variable 0- 3
CaCO ₃	Various	5.0

Weathering plaques were prepared by compounding 70g of compound in a Brabender[®] torque rheometer with a Sigma[®] mixing bowl and #6 rotors at a bowl temperature of 180° C and rotor speed of 80 rpm for 3 minutes after maximum torque (fusion). The samples were then milled through a 2 roll mill at 196° C, then molded into a 7.62cm x 7.62 cm x 0.32 cm plaque and cooled for 6 minutes.

The plaques were placed in a Q-Lab Corporation QUV accelerated weatherometer with UVA-340 lamps. The condition was a wet/dry cycle of 20 hours UV light at 50° C and 4 hours condensation at 40 °C.

RESULTS

Figures 1 through 5 give the dE values for each of the compounds tested with data points at 120, 240 and 500 hours. Note that the Y-scale contracts with increasing TiO₂ levels to fully illustrate the spread between samples. Photos 1 through 5 give a visual comparison of the corresponding compounds at 500 hours total weathering.

It can be seen that at 120 hours of UV exposure, the data spread between the formulations are relatively small. However, it is generally accepted that the human eye can see a color change of dE ≥ 1. In that case, the differences between the high iron containing carbonates and the low iron containing carbonates are visually seen at loadings of 0.5 phr and 1.0 phr of TiO₂, with 1.5 phr at the edge of perception.

With increasing time of UV exposure, (240 hours), the differences become striking at all levels except the 3.0 phr of TiO₂ where some samples are within 1 dE and others greater. However, while the NSF range formula allows 3 phr of TiO₂, it is believed that no one actually utilizes such a high level for economic reasons.

At 500 hours, the difference between the low iron and high iron carbonates are obvious in all cases.

The effect of surface treatment is unclear. At lower TiO₂ loadings, there appears to be a beneficial effect of the surface treated GCCs in withstanding discoloration. However at levels of 1.5 phr and above, this effect seems to reverse itself. Of note is that the particular Georgia 3µm surface treated material had a higher measured iron level than the untreated version. This may be due to the effect of metal wear within the surface treatment equipment.

The other treated product studied, VertiCal® 3T, is made by a novel patented process¹⁰ where the material is centrifugally milled at high gravitational forces. This produces a very narrow distribution, with a correspondingly low surface area. A lower surface area should present less iron for reaction. However the vigorous motion in the mill and surface treatment equipment can give rise to more iron contribution from wear. This is reflected in the much higher absolute iron levels measured in the VertiCal 3T sample than the conventionally ball milled Hubercarb® W3N sample milled using ceramic media. Perhaps the type of iron play a role in this comparison, as at lower TiO₂ levels the VertiCal 3T appears to give less coloration, while at higher levels the effect reverses.

Figure 1

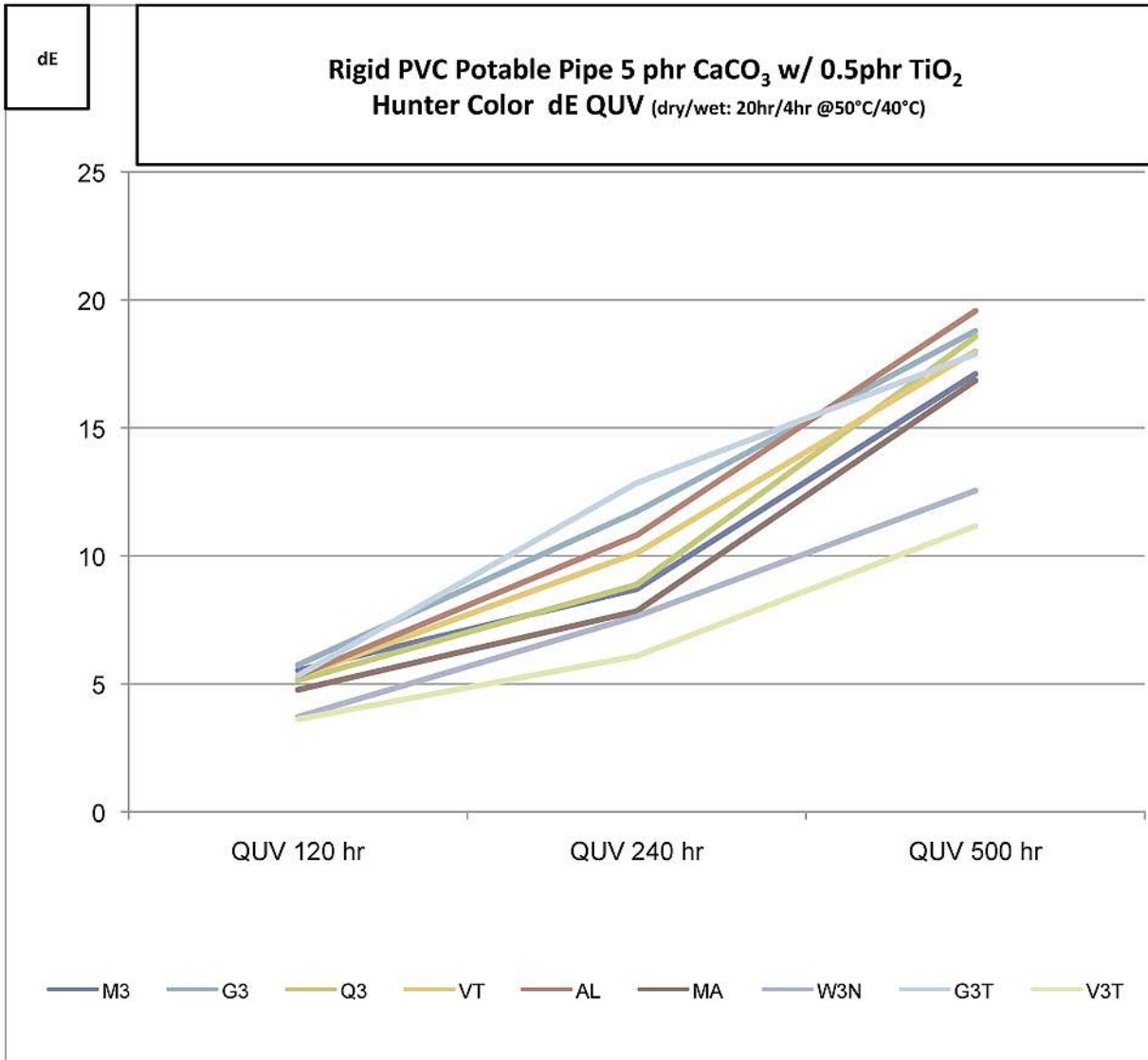


Photo 1

0.5 phr TiO₂ x 500 Hours

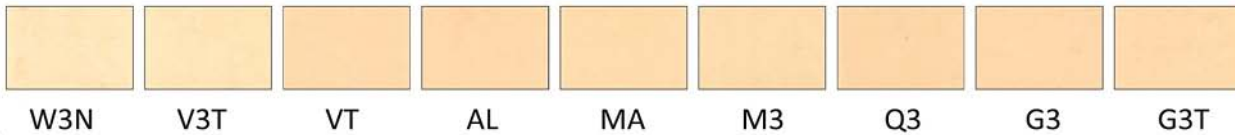


Figure 2

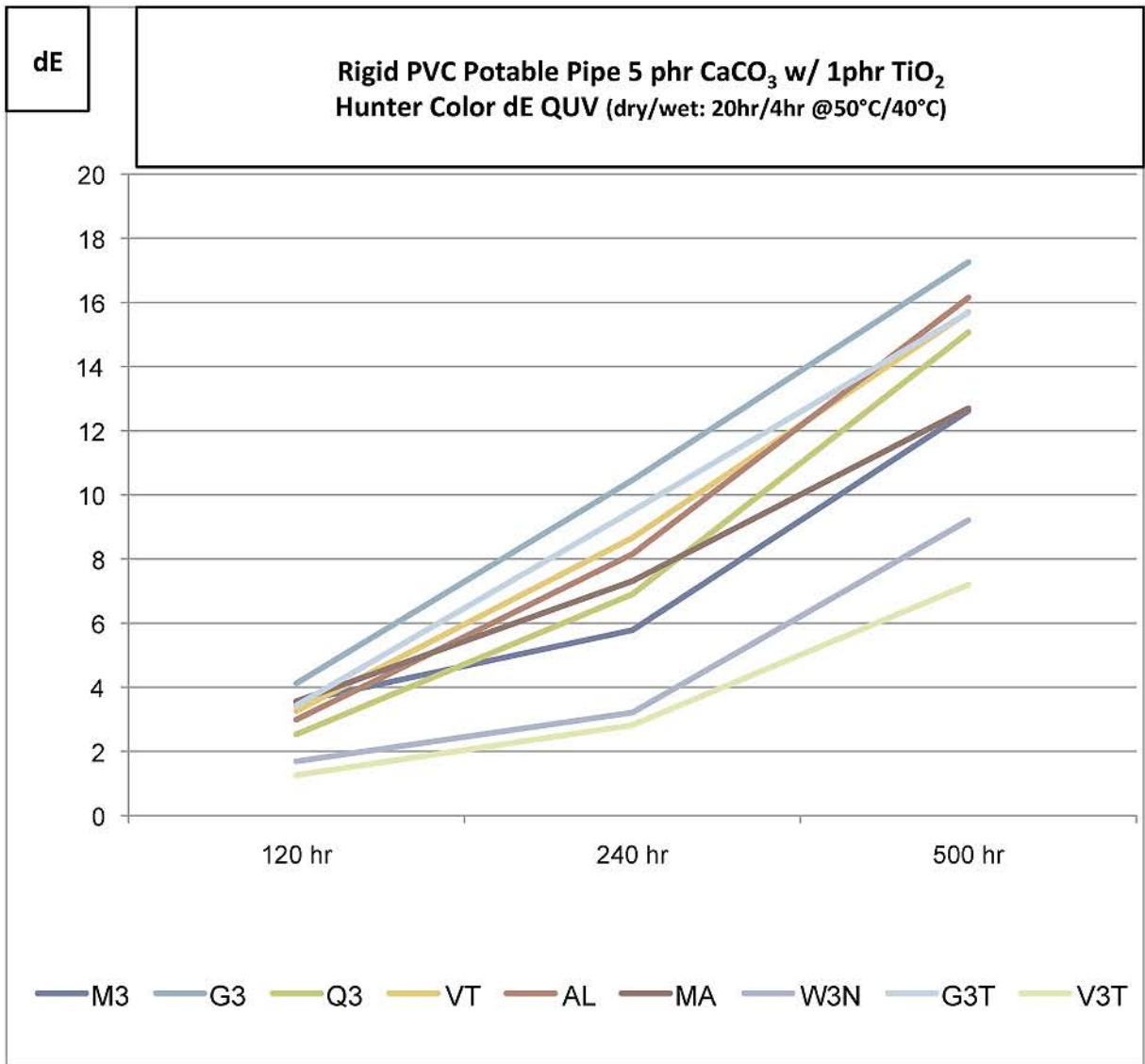


Photo 2

1.0 phr TiO₂ x 500 Hours

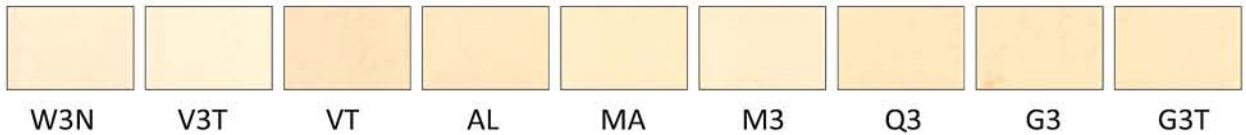


Figure 3

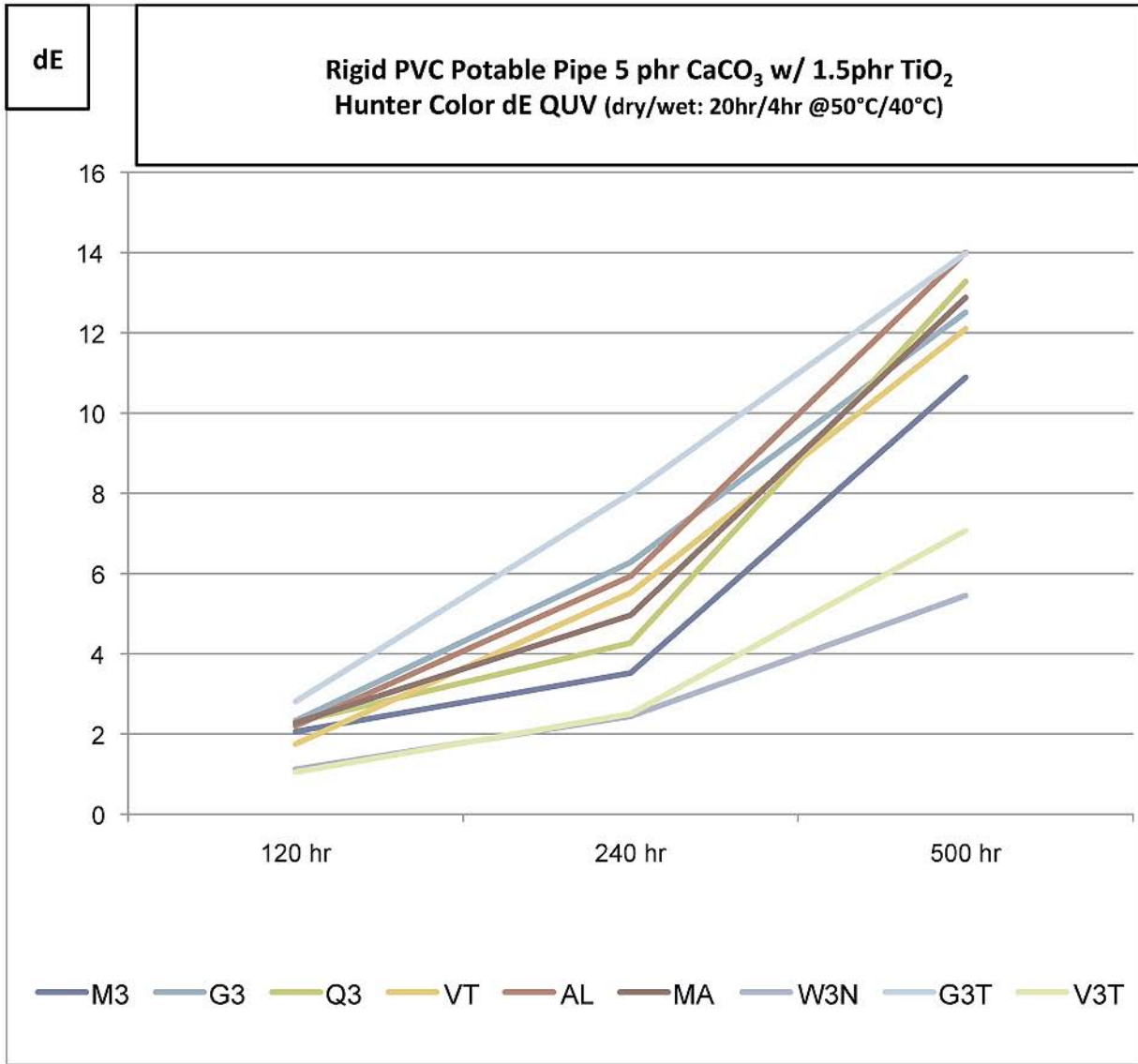


Photo 3

1.5 phr TiO₂ x 500 Hours



Figure 4

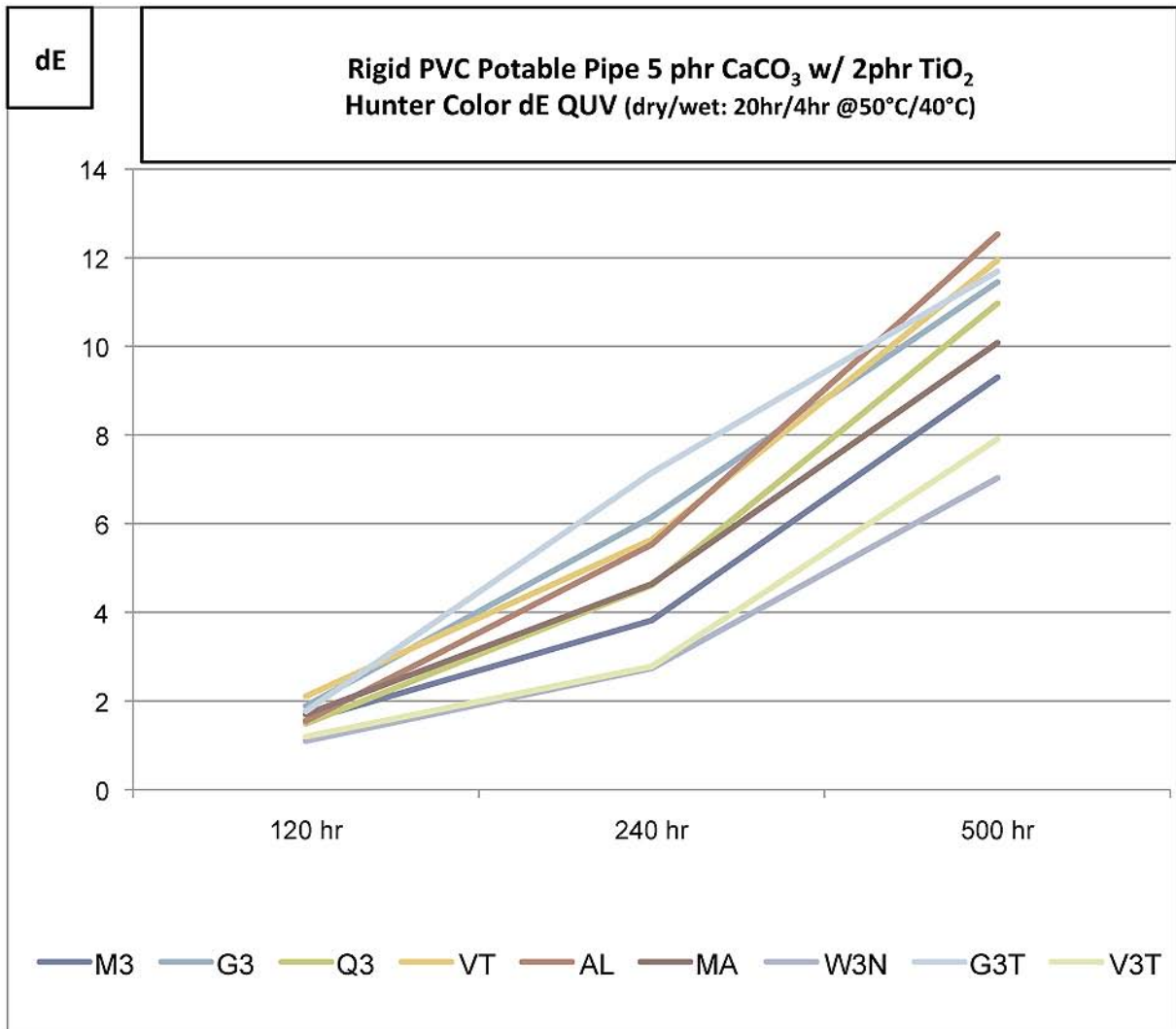


Photo 4

2.0 phr TiO₂ x 500 Hours



Figure 5

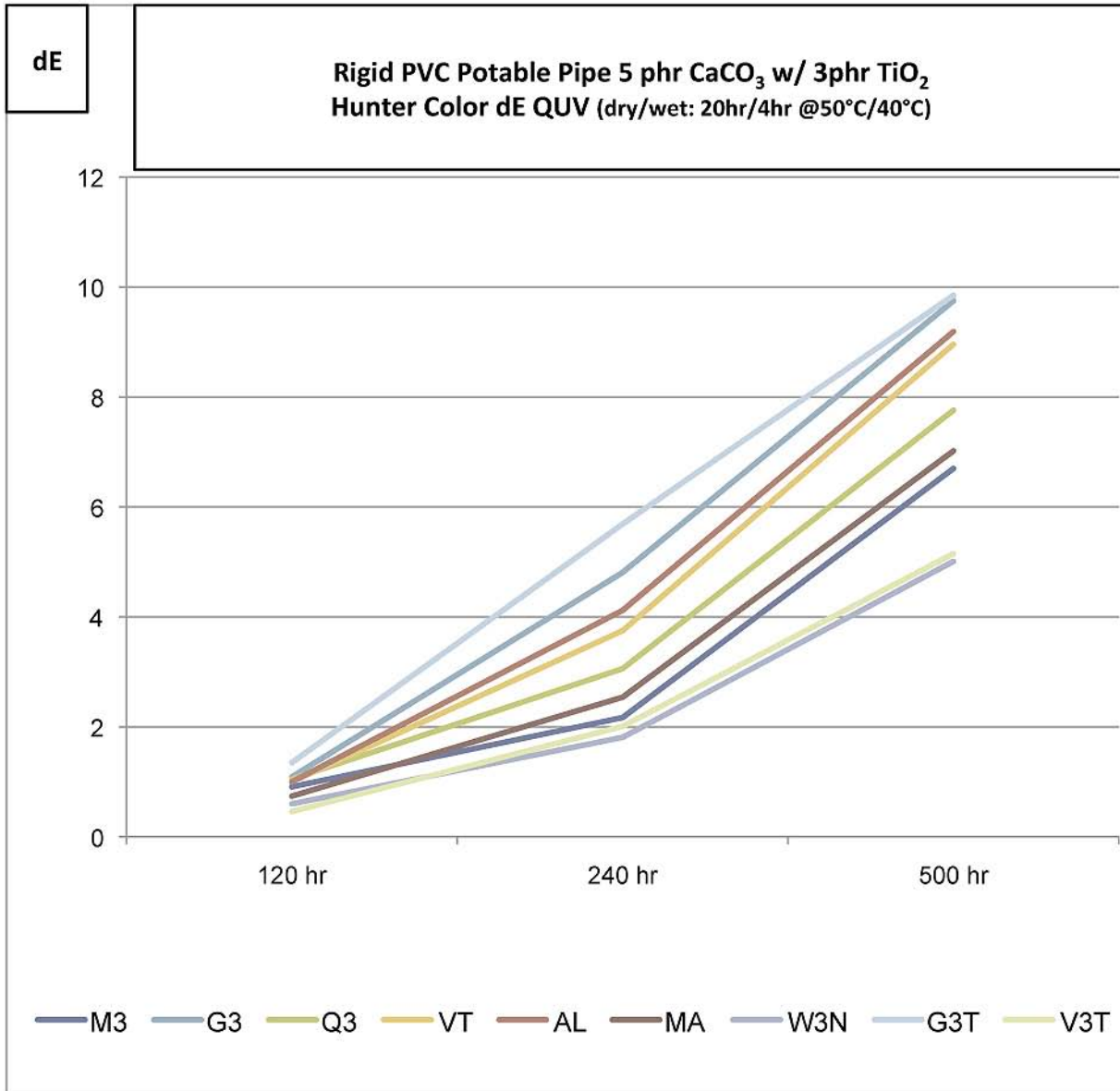
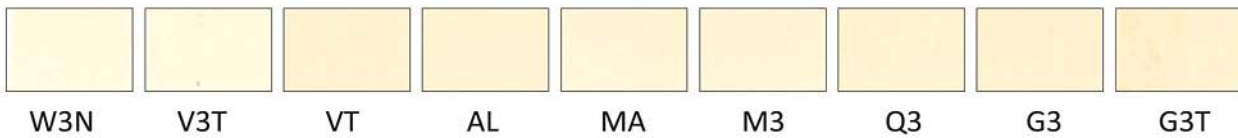


Photo 5

3.0 phr TiO₂ x 500 Hours

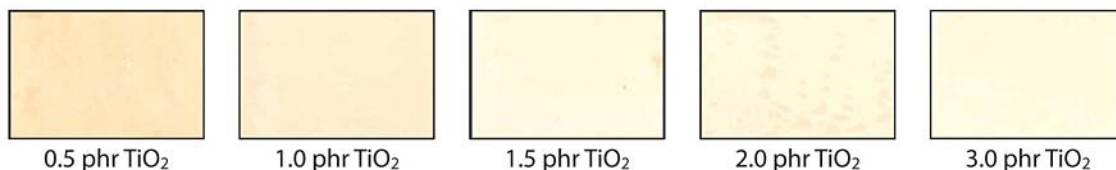


DISCUSSION & CONCLUSIONS

From the experimentation and results, we can reach several conclusions:

- The role of TiO_2 in preventing UV degradation in PVC pipe is confirmed. Higher loadings of TiO_2 are more efficient in preventing degradation than lower levels, as illustrated with the Hubercarb[®] W3N at 500 hours QUV exposure below:

Hubercarb[®] W3N Calcium Carbonate at Various TiO_2 Levels



- The concentration of iron in GCC can predict color change upon PVC pipe exposure to UV radiation. Higher iron levels cause increased color development versus lower iron levels.
- The effect in lower TiO_2 containing formulations (PVC pipe) is more pronounced than with higher TiO_2 containing formulations.
- The effect increases significantly as exposure time increases.
- The use of low iron containing GCC may reduce the amount of TiO_2 required to prevent unacceptable UV discoloration in PVC pipe.

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