Heavy Duty Glass Flake Coatings for Arduous Anti-Corrosion Service.

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ABSTRACT

Glass flakes have been used for a number of years to reduce gas and moisture vapour diffusion through coating and paint films. Advances in glass flake production over more recent years, have allowed thinner and more consistent flakes to be produced. This has led to investigative work into the properties that can be attained by way of using glass flake as a performance improver. The work has investigated many materials both organic and inorganic and in many areas of use – such as tyres and even cosmetics. But, the biggest field of application is in organic resinous materials, not least of which, are those used in the area of corrosion protection for arduous service. Surprisingly, although the thin flakes (below 2 microns) are better performance improvers in most applications in some applications thick flakes (over 5 microns) are found to give better results.

The high aspect ratio of a flake compared to fibres or granular fillers imparts unique properties to materials to which they are added but great care has to be taken in choosing addition level, thickness and size distribution to obtain the required result and for the optimisation of a particular characteristic. This work is tedious, time consuming and expensive but endeavour and patience can be amply rewarded.

Areas of interest where the addition of glass flake can make significant improvements include; fire retardancy, mechanical reinforcement, UV light resistance, Tg and heat distortion, reduction in moisture vapour or gas percolation. Changes in the properties of thixotropy and viscosity, abrasion resistance, dimensional stability. Improved properties can be achieved not only in thermoset and thermoplastic materials such as unsaturated
polyester, polypropylene and PTFE but also in materials such as paper and cement. However, these properties are combined to the greatest effect in paints and coatings used for corrosion protection and in particular heavy duty barrier coatings. Coatings produced using this technology have been shown to give outstanding performance and these have been used in industry, sometimes with good and sometimes exceptional result.

INTRODUCTION

There are many fillers and pigments used in the paint and coatings industry. Some of these are useful as corrosion inhibitors, some as simple extenders to reduce resin cost, some to enhance mechanical properties and some simply as a colourant. Glass flakes do not add colour (except when they are themselves coloured) and rarely can they be classed as extenders except in high cost resins where they may not only improve performance but also reduce cost. But they do give significant performance improvements in nearly all instances where they are correctly used. Other materials cannot and do not do this in the same way. Glass fibre for instance, although giving improvement for stiffness when used at the required volume, barely reduces moisture vapour transmission or fire retardancy. However when glass flake is used as a substitute for the fibre, not only is the modulus and fire resistance substantially increased but also significant reductions in moisture vapour transmission and gas diffusion are achieved.

Apart from component parts coatings, the bulk of coatings and paints used are based on organic resins, however all organic coatings will, to some extent or another, convey moisture vapour and accept gas diffusion. Preventing or resisting this is desirable and it is in this area that glass flakes initially found their niche.

Particles of a high aspect ratio (low thickness to surface area) for instance platelets or flakes, can overlap each other and present a barrier to the passage of moisture and gas diffusion in a film by extending the path length through it. Particles of a granular or spherical nature do not overlap and offer very limited resistance. The high aspect ratio (barrier) fillers are therefore highly desirable for performance improvement.

The benefits of using flake-like barrier pigments, such as mica and micaceous iron oxide in anti-corrosive paints and coatings to reduce moisture vapour transmission have been known for a many years. Other flake pigments with varying attributes such as aluminium and zinc have also been used as combination chemical and barrier fillers with varying degrees of success.

Glass flake introduced into coatings around 1960 gradually gained popularity for several reasons. Glass flakes have a large aspect ratio and unlike mica they are not stepped, are totally impervious to moisture vapour and consistent in composition. Other barrier materials commonly used are opaque and often strongly coloured. Micaceous iron oxide in particular makes coatings and paints difficult to tint in light shades whilst glass flake is clear. Not only that glass flake is chemical resistant and inert in most environments, has good mechanical properties and is generally considered a simple dust hazard or non-hazardous particularly when compared with fibres.

Early glass flake coatings were somewhat crude trowel or brush applied materials basically designed as a fibre glass composite layer but with the glass flake substituting for fibre. It was the late seventies before good spray applied glass flake coatings were available and these were generally thought to be difficult to apply and expensive. They were produced predominantly with unsaturated resins used previously for hand lay up. Epoxy formulations containing glass flake only came later and until more recent times were few and far between. They are now an important sector of the barrier coating market.
From the early eighties glass flake coatings started to become more acceptable, as the performance and benefits of long life became apparent. At the same time prices compared with other coatings dropped, leading to greater acceptability within the market place. It was during this period that research was carried out into the use of glass flake as a performance improver and the types of paint and coating using it multiplied significantly. Unfortunately, the effects of using different flake concentrations, flake thicknesses, differing aspect ratios and the unusual effects on viscosity and critical pigment volume concentration were rarely understood. There was also poor understanding of how the glass bonded within the various resin matrixes. This is still true today of many of the companies utilising glass flake as a filler material. Sometimes the incorrect use of flake though the lack of knowledge leads to a worse rather than better product but often it just leads to poorer than expected results. However, where proper and diligent research is carried out, the glass flake in conjunction with a suitable resin, can give tremendous improvement and allow coatings to work where failure would otherwise occur. Today many different types of paint or coating resin carrier are used with glass flakes, including but not limited to Polyesters, Epoxies, Chlor-Rubbers, Alkyds, Coal Tars, Vinyl's and water based Acrylics.

**BASIC PARAMETERS**

It is important to understand that although the glass flake is impervious to moisture vapour and gas diffusion it does not present a continuous barrier in a resin matrix. The resin carrier therefore plays a very important role i.e. glass flake cannot make a poor resin film into an excellent coating, although it may substantially improve it, but even excellent resins can benefit from addition of flake and performance considerably improved. In addition flake offers differing aspects of mechanical reinforcement than those attained by adding granules or fibre. Notably, by way of horizontal shrinkage reduction during polymerisation on a substrate, reducing coating and coating to substrate stress.

The addition of flake will generally improve the moisture vapour transmission resistance of almost any coating film or membrane and there may be other benefits with new properties being imparted or improved. However, the level at which the glass flake should be added, the particle size distribution and adhesion to the carrier is of paramount importance.

Although glass flakes with aspect ratios as low as 10:1 will give benefit generally the higher the aspect ratio the better the barrier presented. This premise has however to be tempered to some extent, as out of alignment large aspect ratio flakes can afford a direct path through the film where the film is less in thickness than the nominal planar size (diameter) of the flake or cause stress raisers for crack propagation. In addition there are some properties that may be adversely affected when using large flakes such as flexibility and elongation to break. Also for consideration, is the practicality of using large planar size flakes i.e., when a coating has to be sprayed the gun tip size is limited by several factors and the flake needs to be small enough to pass through the spray tip. Large flakes also tend to produce rough surface finishes. It is therefore common, that flakes of around 500um and below are used for spray application and flakes above this size i.e. as large as 1500um are rarely used except for hand applied materials. When compounding flake into thermoplastic materials there are several considerations but it
has generally been found impractical to incorporate flakes with a planar size greater than 300μm and most usage has been with flake of circa 180μm or below.

Flake size and thickness are only one of the issues involved in obtaining performance. The quantity of glass flake added and particle distribution is also critical. It is obvious that if thin flakes of glass are used there are many more flakes than if thick ones are used for the same weight, and therefore the surface area to be wetted with the thin flakes is vastly greater. This means that it is impossible to just simply state the requirement for an amount of flake as for instance 20% by weight. It may be possible to add 20% by weight of flake at a thickness of 5 μm and not exceed the critical pigment volume concentration to resin ratio (CPVC). If the same quantity by weight of a flake at 2 μm thickness were added, then the surface area of this flake will be at least two and a half times that of the thicker one and there may be insufficient resin for wet out thus the CPVC level is exceeded. In any case the viscosity may be so high when changing from the thick flake to thin flake that addition at the same weight becomes impossible.

It is obvious from the preceding statements that once a thickness of flake has been chosen it is important to optimise the addition level. That level will depend upon the type of resin being used and what other pigments or fillers are being used in conjunction with it. A further consideration is whether or not coupling or bonding agents are used to provide better adhesion of the glass flake to the resin and the substrate. Adhesion plays a substantial role in the performance of organic materials in corrosion protection. The bonding of fillers into the resin is also a very important facet in obtaining performance both from a corrosion resistance point of view and in mechanical performance. Silanes have been used for many years in the glass fibre industry to improve bonding and in consequence performance. This improvement in performance is seen both as an increase in some of the mechanical properties and a decrease in moisture vapour transmission. In thermoset resins it is possible to get substantial improvements in performance simply by adding the silane chosen to the resin component either just before or just after the glass flake is added. With thermoplastic materials however this is generally not possible and the glass flake has to be pre-treated with silane. It is noticeable that pre-treated flake will improve the bonding performance in thermosets to a higher level than that achievable by adding the silane indirectly via the resin.

Where the silane is added to the resin, it is observed that there is a critical level and the optimisation peak is often very steep. This is true for each particular resin, glass thickness, particle distribution and addition level, it should also be noted that other fillers or additives such as thixotroping agents will affect the optimisation level. Where the silane is added by pre-treating the glass then the level of silane used is not so critical, provided that saturation of the flake, causing agglomeration, is not achieved. It is also observed that with pre-treated glass a much higher level of glass flake can be added to the resin and in particular to thermosets without exceeding the CPVC level. One downside of using pre-treated flake however, is the cost and a possible change in safety hazard classification.

It seems fairly obvious from the foregoing that barrier pigments with high aspect ratios and in particular glass flake cannot simply be added at a nominal value if good results are going to be obtained. Specifiers of coatings containing glass flake often state the minimum loading of glass flake and a thickness for the product to be applied at, but what knowledge do they base this on?
Even if the characteristics of a particular resin and formulation are known, product formulation rather than performance specification can be dangerous. For example a specification could state 'Epoxy with a minimum glass flake loading of 20% by weight. This level of addition could in many formulations exceed the CPVC level and the coating would therefore give better performance at lower glass flake loadings. In addition neither the flake thickness nor planar size nor particle size distribution is specified. It is therefore possible that a coating with very high performance could be precluded from being used under such a specification regime whilst a poorly performing material met the criteria. It is more sensible therefore, that performance criteria rather than formulation criteria are specified.

With new production methods glass flake can be produced for various purposes at consistent thickness from around 10 urn to as low as 100 nanometres and almost limitless particle size distributions are possible. The effects of thickness, particle size, volume concentration etc., were evaluated in glass flake coating formulations using flakes of differing thickness and diameters and with differing particle distributions. Some of the results were surprising, others expected and because testing was carried out over a wide range of properties and not just diffusion and corrosion resistance, some interesting parameters were discovered. Of particular interest was the amount of fire resistance provided when using glass flake, a reduction in smoke emissions, heat distortion and creep, and reduction in shrinkage during polymerisation, especially in the horizontal plane. These results led to work also being done on non coating applications and engineering thermoplastics.

**EXPERIMENTAL**

Evaluation of various coating materials, thermoset resins and composites was undertaken.

**Test Involved**

- Moisture Vapour Transmission (MVT).
- Water Absorption.
- Modified Atlas Cold Wall (Osmotic Blister) Testing
- Cathodic Disbondment
- Glass Transition (Tg) (DSC) and (DMTA)
- Fire and Flame Spread Resistance.
- Abrasion Resistance.
- Chemical Resistance
- And a variety of Mechanical Tests.

Some of the test work conducted and the results are shown it has not been possible to show the full set of tests or the results obtained.
EVALUATION OF FLAKE PLANAR SIZE ON PERFORMANCE

Tests were carried out to evaluate the mechanical performance of a glass flake filled polyester system with flake thickness nominally 2.7um and two different nominal planar sizes, these being a D50 of 180um (1) and a D50 of 575um (2). The loading was 15% by weight in each case. See Table 1.

TABLE 1

<table>
<thead>
<tr>
<th>TEST</th>
<th>TEST METHOD/STD</th>
<th>RESULT 1 180um</th>
<th>RESULT 2 575um</th>
</tr>
</thead>
<tbody>
<tr>
<td>COMPRRESSIVE STRENGTH</td>
<td>BS 6319: Part 2: 1983</td>
<td>632 kg/cm² 8984 psi</td>
<td>359 kg/cm² 5051 psi</td>
</tr>
<tr>
<td>FLEXURAL PROPERTIES</td>
<td>BS 2782: Part 10: Method 1005 : 1977 (three point method)</td>
<td>164.6° @ 0.85 kg (1.87 lbs)</td>
<td>171.4° @ 1.1kg (2.43 lbs)</td>
</tr>
<tr>
<td>% ELONGATION TO BREAK</td>
<td>BS 6319: Part 7: 1985</td>
<td>0.6%</td>
<td>0.05%</td>
</tr>
<tr>
<td>ADHESIVE STRENGTH</td>
<td>BS 3900: Part E10</td>
<td>132.3 kg/cm² 1882 psi</td>
<td>79.38 kg/cm² 1120 psi</td>
</tr>
<tr>
<td>SHEAR STRENGTH</td>
<td>BS 6319: Part 4: 1984</td>
<td>198 kg/cm² 2821 psi</td>
<td>208 kg/cm² 2953 psi</td>
</tr>
<tr>
<td>HARDNESS</td>
<td>ASTM D-2583</td>
<td>40.0 Rockwell H 38.2 Barber Colman</td>
<td>52.0 Rockwell H 43.2 Barber Colman</td>
</tr>
<tr>
<td>IMPACT STRENGTH (Drop Weight)</td>
<td>BS3900: Part E3: 1973</td>
<td>9.5 J (Nm) Forward 2.0 J (Nm) Reverse</td>
<td>8.2 J (Nm) Forward 2.0 J (Nm) Reverse</td>
</tr>
<tr>
<td>ABRASION STRENGTH</td>
<td>Taber H – 18 1 kg weight 1000 cycle</td>
<td>435 mg loss</td>
<td>415 mg loss</td>
</tr>
<tr>
<td>HEAT DISTORTION TEMPERATURE</td>
<td>Differential Scanning Calorimetry (DSC)</td>
<td>92°C 197.6°F</td>
<td>96°C 204.8°F</td>
</tr>
<tr>
<td>LATERAL CURE SHRINKAGE</td>
<td>COR102</td>
<td>8.5%</td>
<td>3.9%</td>
</tr>
</tbody>
</table>

Test data obtained at 20 Deg C on standard cure.

It is interesting to note the substantial reduction in cure shrinkage found when using the larger flake, the significant difference in compressive strength and elongation to break. These effects caused simply by increasing the aspect ratio of the flake.
EVALUATION OF VARYING FLAKE CONCENTRATION

Tests were carried out to evaluate the change in moisture vapour transmission afforded by varying the flake concentration. A vinyl ester resin was used as the carrier resin with the only difference in the materials tested being the addition level of glass flake. Tests were conducted initially to zero in on the area of criticality, then levels of 14%, 15% and 16% by weight were used to carry out the main evaluation.

TABLE 2
TESTED IN ACCORDANCE WITH ASTM D1653

<table>
<thead>
<tr>
<th>glass flake concentration by weight</th>
<th>average result of 5 samples Perm inches $10^{-5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>14%</td>
<td>10.61</td>
</tr>
<tr>
<td>15%</td>
<td>3.46</td>
</tr>
<tr>
<td>16%</td>
<td>3.64</td>
</tr>
</tbody>
</table>

As can be seen from these results the quantity versus permeation curve is very steep with a 1% change in the addition level changing the permeation rate from 10.61 to 3.46. A further addition of glass changes the permeation rate for the worse but only marginally with further additions (not shown here) showing a progressive worsening as the CPVC level is approached and exceeded. Subsequent additions show a rapid increase in MVT. This steepness of the MVT performance curve is not always so high. In some instances the curve is a gradual slope at both ends with a flat bottom. This type of addition/performance curve is preferred as this allows not only some deviation for production tolerances but it also allows the formulator to look at other properties i.e. mechanical or fire retardancy, without compromising the other aspects. Glass at a thickness of approximately 5um allows an addition of some 24% and has an optimum reduction in MVT at around this level. Whereas glass at a thickness of approximately 2.2um can not be added above 20% loading without detrimental effects but has a MVT rate reduction almost a magnitude better than the 5um flake and this is achievable over the range of approximately 14 to 18%.

CATHODIC DISBONDMENT TESTING

The test evaluates electrical resistivity, moisture content, adhesion to the substrate and alkali resistance all in conjunction. Each of the four aspects if adverse will effect the end result. The same variations in glass loadings were evaluated for Cathodic Disbondment in the same resin matrix as those above and the results are shown below.

TABLE 3
CD TESTED TO BS3900 F11

<table>
<thead>
<tr>
<th>glass flake concentration by weight</th>
<th>average of 3 tests disbondsment</th>
</tr>
</thead>
<tbody>
<tr>
<td>14%</td>
<td>5.0 mm</td>
</tr>
<tr>
<td>15%</td>
<td>3.4 mm</td>
</tr>
<tr>
<td>16%</td>
<td>4.9 mm</td>
</tr>
</tbody>
</table>
The results show a similar pattern to that of the moisture vapour transmission tests except that in this instance the 16% result is nearly as bad as the one at the 14% level.

**EVALUATION OF BONDING AGENT LEVEL**

In order to evaluate the addition levels of the organo-functional silane bonding agent and its criticality, a standard vinyl ester glass flake formulation was used with the level varied. Tests were then carried out to evaluate the performance of each cured sample.

As can be seen from the table overleaf, the addition level of 0.6% Silane improves the performance of the coating considerably. It is interesting to note that although the bond strength is slightly better on the 0.95 level in all other respects the properties are very similar to those of the 0.2 addition level. Some of the test work showed initially worse results with silane addition over no addition until the level was further increased.

**TABLE 4**

ADHESION EVALUATION VINYLESTER COBALT/DEA/MEKP CURE. (glass flake 15%)

<table>
<thead>
<tr>
<th>Level</th>
<th>A 0.2% Silane</th>
<th>B 0.4% Silane</th>
<th>C 0.6% Silane</th>
<th>D 0.8% Silane</th>
<th>E 0.95% Silane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Permeability (perm/inch)</td>
<td>1.86 x 10^{-4}</td>
<td>0.41 x 10^{-4}</td>
<td>0.34 x 10^{-4}</td>
<td>1.06 x 10^{-4}</td>
<td>1.63 x 10^{-4}</td>
</tr>
<tr>
<td>Water Absorption (%wt.gain)</td>
<td>0.148 (24 hrs)</td>
<td>0.120 (24 hrs)</td>
<td>0.0345 (24hrs)</td>
<td>0.100 (24hrs)</td>
<td>0.147 (24 hrs)</td>
</tr>
<tr>
<td></td>
<td>0.312 (7day)</td>
<td>0.198 (7day)</td>
<td>0.317 (7day)</td>
<td>0.317 (7day)</td>
<td>0.350 (7day)</td>
</tr>
<tr>
<td></td>
<td>0.512 (14day)</td>
<td>0.447 (14day)</td>
<td>0.435 (14day)</td>
<td>0.444 (14day)</td>
<td>0.486 (14 day)</td>
</tr>
<tr>
<td>Adhesive Strength (kg/cm²)</td>
<td>500</td>
<td>587</td>
<td>625</td>
<td>585</td>
<td>557</td>
</tr>
<tr>
<td>7 Day Barcol Hardness</td>
<td>49</td>
<td>50.2</td>
<td>51</td>
<td>49.7</td>
<td>49</td>
</tr>
<tr>
<td>Bend Test – Angle coating Cracked</td>
<td>11°</td>
<td>16°</td>
<td>20°</td>
<td>14°</td>
<td>10°</td>
</tr>
</tbody>
</table>
EFFECT OF PARTICLE SIZE DISTRIBUTION ON BLISTER RESISTANCE

Further test work was carried out to evaluate any change in performance by altering the particle size distribution. The test work was carried out by using micronised glass flake with a thickness of approximately 2.2um and a nominal planar size of 80um and a D50 of 50um in a resin formulation and comparing it with a formulation which contained the same quantity of flake but which had a different particle spread e.g. D50 of 35um. Evaluation of performance was carried out by using a modified Atlas cold wall cell with demineralised water and a temperature gradient across the film of approximately 60 Deg Centigrade.

The test results showed that the formulation with the smaller glass flake (D50 = 35um) had worse performance than the existing coating (D50 = 50um). This was shown by the extent of osmotic blistering. Formulations were then produced with the glass being blended. A significant performance improvement was achieved when the glass was blended at a ratio of approximately 60/40 (being 60% of the D50 = 50um, 40% D50 = 35um) with the test panel showing no osmotic blistering occurring at all where previously both panels had shown blistering.

EVALUATION OF THIXOTROPIC PROPERTIES

Tests were made to evaluate the differences in viscosity and thixotropic properties of a standard coating formulation using glass flake. Work was carried out using glass flake at a thickness of circa 5um and 1.3um. It had been apparent from previous test work that the thinner the glass flake the more surface reactive it appears to be, to the extent that flake of a thickness below 1um can be bonded together dry simply by using a light pressure. This reactivity seems to come from hydroxyl groups on the glass surface. When the glass flake is first manufactured there is no moisture on the surface. This is obviously a good point at which to apply the silane-bonding agent if any is to be used (although some silanes require moisture for bonding).

As the glass ages over a few days moisture is adsorbed onto the surface and there is a slight weight gain coupled with a drop in reactivity. This moisture can only be driven off by using temperatures in excess of 360 Deg C but on cooling moisture will reattach over a period of a few days if left exposed to atmosphere. The moisture uptake will vary with surface area and the number of hydroxyl groups on the surface so this weight gain can be used to give some measure of surface reactivity. From evaluations the thinner glass flake has always shown substantially greater reactivity than the thicker glass flake independent of surface area.

Although not considered as a thixotroping agent it was thought that there may be some synergistic effect capable of being used to benefit thixotroping. For instance in reducing the amount of fumed silica within a coating film.

A standard formulation containing 5um flake was used as a reference material, the viscosity, thixotropic index and hold up on a vertical surface being measured. Various formulations were then produced with 1.3um thick glass flakes. The Brookfield viscosity and thixotropic index were measured and a reduction in the fumed silica thixotroping agent made to compensate. The formulation which produced the nearest viscosity and spray characteristics was then used for further evaluation. The viscosity's, thixotropic index and hold-up thicknesses are shown below.
Table 5
HOLD-UP COMPARISON

<table>
<thead>
<tr>
<th></th>
<th>Viscosity 5/50 rpm</th>
<th>Thixotropic index</th>
<th>Hold Up um.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5µm glass flake</td>
<td>21,000/84</td>
<td>2.5</td>
<td>550um</td>
</tr>
<tr>
<td>1.3µm glass flake</td>
<td>34,000/97</td>
<td>3.54</td>
<td>700um</td>
</tr>
</tbody>
</table>

The glass flake level in the second formulation was reduced by 4% over that of the one containing 5µm glass but is estimated to have a surface area more than twice that of the original formulation. The thixotroping agent, fumed silica was also reduced by 50% for the second formulation, demonstrating the thixotroping properties of the thin flake and giving a value to it.

PROCESSING/MIXING TIME

One of the areas which greatly affects the performance of the glass flake within the carrier is the mixing time used after all flake is in the resin. Mixing time affects both wet-out, distribution and ultimately break-down of the flake, having significant impact upon not only MVT rate but also the mechanical properties of the resultant coating. Tests were carried out to evaluate the parameters using an unsaturated polyester resin and different grades of flake, compounding of the glass flake into the resin was done using a Z-blade mixer. The test results showed that mixing times for optimum product performance vary significantly dependent upon flake thickness, particle size and addition level (amount). The smaller planar size flakes required a longer mixing time than the other flakes with larger aspect ratios.

Microscopy shows that the samples contained poorly dispersed flakes after 45 minutes mixing but even distribution of the flakes after 60 minutes, and subsequent micrographs taken of specimens that had been mixed for 75 and 90 minutes show breakdown of the flakes occurring.

Overall, the higher the flakes’ apparent volume content in the specimen, the better the mechanical properties that specimen provides, given that satisfactory mixing is achieved.

Once the parameters in the preceding are understood, what can be achieved even with relatively small additions of glass flake can be quite startling. It was shown in a test in Prague University in 1990 that a service tolerant coating that had 3% glass flake added to it substantially improved in substance over the solely granular filled material. This enabled the product to be used in areas where previously it would not satisfy the duty requirements and considerably extended the market potential.
The preceding work and evaluations show that there are and substantial benefits gained from using glass flake barrier pigmentation and several properties that can be achieved that cannot be obtained with other fillers. There is however a need to ensure that the formulation is specifically tailored for optimum performance. It is no use simply adding arbitrary amounts of arbitrary thickness and arbitrary particle size glass flake and of course the type and amount of bonding agent will vary not only with resin type but the surface area of the glass flake within the formulation.

There are some negative aspects in using glass flakes, these relate primarily to reverse impact resistance, stiffness and cost although not all materials are affected in this way. The cost of flake glass in some applications can some times prove prohibitive but in most cases the improved performance more than justifies the additional cost and when whole life cycle costing is taken into account they can nearly always be the lowest cost.

Looking at coatings to give performance in oilfield service and particularly in production areas care has to be taken to get high performance and this is a never ending research and development task. There are fewer coatings that perform well at high temperature, so more care is required in selecting coatings for use in environments that will see temperatures above 60°C. It is even more difficult to select coatings that will see immersion service above 95°C.

**OPTIMISING THE TECHNOLOGY**

Corrocoat has over the last 15 year been researching the use of various resins to obtain higher temperature, corrosion resistance performance, in combination with chemical resistance and ease of application in the field. The latter being of paramount importance for all but a few applications. There are some exotic materials that perform well at temperature but need extensive heat post cure, not practical in the field, and sometimes laboratory type application conditions, these were excluded.
It was thought that by taking a technologically advanced resin system, that in it's own right gives excellent chemical and temperature performance, then enhancing that performance utilising the foregoing glass flake knowledge to get it even better, that, would allow us to give corrosion protection in many areas covered only by expensive and sometimes ineffective metallurgy at present. Vinyl esters have been used to excellent effect for many years and have slowly improved in performance. But non the less, this resin is generally restricted in aqueous immersion to circa 90C and something better was required.

With the above parameters in mind research was carried out into epoxies of various types and using various cures, high temperature vinyl esters, sol-gels, organic/inorganic mixtures and hybrid or polymer alloy resins. This research has been carried out over a number of years and materials were not evaluated simultaneously. Although some resin systems were obviously not suitable from the outset general test parameters were set.

The resins were tested on their own (no fillers or thixotrope) for Tg and MVT rates at what were thought to be suitable thicknesses for the material concerned. They were then tested in immersion using Atlas Cold Wall test cells at ambient pressure and temperatures of circa 90C with tap water. Where a resin looked promising i.e., it did not have extensive cracking, delamination or blistering it was formulated into a coating using thixotrope and glass flake. The levels of glass flake etc, the coupling agent, curing agent etc., were varied to evaluate performance improvements or deterioration. These materials were then tested in pressurised Modified Atlas Test Cells at temperatures gradually increasing from 110C upwards but mainly at 150C (the aqueous immersion limit of the existing 'in use' formulation) and then 180C.

Some of the evaluation work is listed below:

**Phenolic Epoxy Novolac/ BF₃ Cure**

BF₃ Activator used in conjunction with a Phenolic Epoxy Novalac Resin was tried. It was hoped that this system would form ether linkages which would give rise to a more temperature resistant coating. This system requires a 75°C post cure which was considered practical in the field. However, when immersed in water at 150°C this material cracked significantly and de-laminated after one week.

The BF₃ accelerator was then blended with another epoxy resin in an attempt to create enough exotherm heat in the epoxy/amine reaction to initiate the epoxy/BF₃ reaction. This did not improve the performance of the system. Several trials on this theme resulted in no useable materials.

**Silanol Functional Resin**

A high temperature resistant silanol resin was filled with calcined alumina, glass flake and a range of different pigments (TiO₂, red iron oxide, black iron oxide, green chromium oxide) in attempts to polymerise the resin at ambient temperature.

However, these materials could not be made to cure at room temperature and it was decided to evaluate with cures at high temperature. Following a cure at 130°C the various
coatings were immersed in water at 150°C. The best coating was in an unacceptable condition after only one week.

**Phenolic Epoxy Vovalac/Silanol Functional Resin System**

A Phenolic epoxy Novalac/Silanol resin blend was made. This resin blend was filled with glass flake and calcined alumina. When subjected to immersion in water at 150°C the coating was found to fail in some areas after one week but large areas of the plate were found to be in an acceptable condition. Fumed silica was incorporated into the formulation to create a more stable and homogenous base. This formulation was post cured for 8 hours at 80°C and subjected to immersion in water at 150°C for four weeks. This coating withstood these conditions and was in an acceptable condition afterwards but was showing signs of impending failure. In an attempt to further improve the extent of cure of the silanol component within this system cobalt octoate incorporated into it. The resulting coatings performed worse than the formulations containing no cobalt octoate.

Different resin blends were incorporated into the system as it was claimed by the resin manufacturer that a blend of two different types would give rise to a better cured film. The resulting coating was extremely brittle. It cracked and delaminated under immersion in water at 150°C after just one week.

Initial adhesion results for the best formulation were very low averaging around 600psi but removal of calcined alumina from the formulation increased the adhesion value from 600psi to 1200psi. A temperature/cure study was conducted by coating Atlas Cell plates and curing these coatings individually at 80°C, 70°C, 60°C, 50°C and ambient temperature (approx. 20°C). Coatings cured at ambient temperature performed as well as 80°C post cured samples when immersed in water at 150°C. However all failed after several weeks immersion. It was decided to try and optimize the film thickness and test again. The initial formulated material was applied at a range of WFTs from 300μm - 2000μm and immersed in water at 150°C.

**Silane Trials EPN/DC 805/A2410B75 Resin System**

A range of silanes were incorporated at 0.01%, 0.05%, 0.1%, 0.5%, 1.0% and 1.5% into the formulation in an attempt to improve adhesion of the resins to the filler particulates and substrate. These were:

- 3-glycidoxypropyltrimethoxysilane
- phenyltriethoxysilane
- aminopropyl triethoxysilane
- Trimethoxysilylvinylsilane
- Tetraethyl orthosilicate
- Polydimethylsiloxane

For the formulation containing 3-glycidoxypropyltrimethoxysilane the adhesion value increased from 1200psi to 1550psi. Formulations containing silane performed worse than formulations with no silane when immersed in water at both 150°C and 180°C. With all formulations containing silane the base gelled within 2 weeks of storage at ambient temperature. Amino functional silanes were incorporated into the activator to avoid the
storage issues but these formulations performed poorly when immersed in water at 150°C.

**Sol Gel**

This system consisted of silica hydrogel (SiO₂) dissolved in potassium silicate solution, treated with methyltrimethoxysilane and zinc dust as the second component of a two pack system. Dilatancy issues were experienced in the manufacture of the base. Extra water was used to overcome this problem. Some zinc dust within this formulation was replaced with glass flake. The resulting coatings performed poorly when immersed in water at 150°C and Intercoat adhesion was poor. They also performed poorly when subjected to salt spray tests. It was hoped that the addition of zinc dust would be sufficient to catalyse the reaction but this appeared not to be the case as formulations containing zinc or zinc and glass flake did not perform better than the formulations containing only glass flake.

**GLASS FLAKE GRADE CHANGES**

It was decided to look at the effect on the grade of glass flake added to some of the formulations previously evaluated to see what the effects were on this system compared with previous knowledge at lower temperature evaluation. The micronised flake within the formulation was replaced by milled flake in an attempt to improve the mechanical and barrier properties. Atlas Cell plates were coated using this formulation change and immersed in water at 150°C. One coating survived for six weeks before failure due to cracking in the non-immersed area only. A noticeable improvement on the previous formulation which survived immersion in water at 150°C for one week.

In order to get a greater glass to resin ratio a much larger glass flake thickness was incorporated into a formulation at a higher percentage in place of the previous flake to reduce the resin content and observe any improvements in cold wall performance. After one month surface cracking was observed in the non-immersed area. After two months slight surface cracking could be observed in the immersed area and the cracking in the non-immersed area had become slightly worse but the coating continued to protect the substrate from corrosion. After three months the coating had deteriorated slightly more in the immersed area and the non-immersed area but continued to protect the substrate. After four months the coating deteriorated further and appeared to have stopped providing corrosion protection in the non-immersed area. Surface cracking could be observed in the immersed area and it was unclear if this coating was protecting the substrate at this stage.

Formulations using the large glass flake at high percentages were found to survive under immersion in water at 180°C for three to four months - a significant improvement over the previous formulations and totally contradictory to extensive previous work that had been conducted.

Using this information the existing in service Vinyl ester/Urethane Hybrid was reformulated with thicker glass (7um) and at a higher loading. Significant performance improvements were observed at the higher temperatures (180°C).

In an attempt to further improve the properties of the coatings evaluated. Formulations were prepared using blends of different glass thicknesses and particle size, as previously
this had shown significant improvement, as mentioned before. Three different filler blends were used but unexpectedly, all three filler formulations at several loadings, performed much worse than the formulations containing only the single size large glass flake.

**Porosity/Bubble Reduction Study**

A lot of work was carried out on removing surface skips and micro voids in the coatings but no performance improvements were made using the various surfactants and bubble release agents tested. After various trials this work was abandoned.

**GENERAL**

Although there were several materials that, theoretically, looked promising, and some survived the initial pressurised Atlas Cell test regime – only one consistently performed at the minimum temperature requirement of 150C immersion, the existing 'in use since 1996' coating. This is a Vinyl ester/Polyurethane Hybrid.

Using some of the information gleaned over the years of trials, the glass size and content was changed in this coating. That gave some performance improvements at 180C allowing a better margin in continuous service in aqueous media at 150C and in non aqueous media as high as 180C. In gas environments the coating has been used and stood the test of time to temperatures as high as 280C.

"This material also tested well in an evaluation carried out in Canada for the “While it is not a definitive method of comparing the coatings, it is interesting to note that there were only two (2) of the thirty-one (31) coatings that had good performance in at least six (6) of the eight (8) tests”

**Service:** The hybrid glass flake coating has been used in various corrosive environments including; High temperature heat exchanger shells, water and condensate environment at between 100 and 160C., Sodium Base exchangers, Salt water environment between 90 and 120C., Aluminium Chlorohydrate Reactor where aluminium is dissolved into HCL and process agitated with steam., Waste gas absorption tower, circa 150C., Flare Stack pre heaters at 180C, Nickel Sulphide quench tank operating between 100 and 140C., demineralised water pre heat tank at 120C., and Crude oil flow lines operating up to 160C., High temperature waste incineration: Waste gas scrubber operating at 200C with excursions to 400C. There are many more examples but the most relevant to the Tar Sands expansion is the examples from the Duri Oil Field in Indonesia.

In the Duri field, the Bitumous Oil is extracted using a mixture of steam and solvent. The ground conditions over and through which the production lines run is considerably variable in pH but can be very acidic and the water table can vary from above ground level to some metres below in the same location dependant upon season and rainfall. This results not surprisingly in the external corrosion rates of the pipe being several magnitudes that of the internal rate. The pipes were generally either coated with a bitumen based coating but many other coatings had been tried or left un-coated which seemed reasonable considering the expense of coating and the short life-span. A particular problem was at Road Crossings where the pipe through necessity was almost
always buried and through wall leaks were reported to have occurred in as little as two and a half months. In consequence the road crossings were not surfaced with tarmac even on paved roads due to the constant necessity to dig out the pipework.

In 2001 coating trials began in earnest at the Duri field. Trials on the external coating of high temp oil flow lines (highest temp found 176 deg C - 348 deg F) with the Vinyl ester/Polyurethane Hybrid glass flake for buried service in 2001 resulted in a trial contract in 2002. After this there was a pause for 2 years whilst the field customer tested a lot of other coatings, all of which failed in a short time period. We have since learned that in another of the customers fields that had normal flow line operating temperatures of only 70 -90 deg C, a dedicated facility had been built, to apply a powder coating for the buried pipe. By the time the facility had been built, the field trial areas coated had already failed and the plant stands empty to this day. Other coatings were tried including two major paint manufacturer’s glass flake coatings, applied to a number of pipes and over a range of service temperatures. All failed within less than a year.

Following the tests our company was called back in middle of 2004 and has been coating pipe on a continuous basis since then. We have coated the high temperature 4” flow lines with Corrothane XT, the Hybrid Coating and the larger diameter, lower temperature pipe with Polyglass VEF, a glass flake vinyl ester coating.

At the end of 2007, 40% of the fields road crossings had been coated. In 2001 the Duri field had approximately 1200 oil leaks. An early pipe replacement program succeeded in getting the leaks down to 250 in 2004 but at a significant capital and down time cost. However, since the introduction of the Hybrid glass flake coated pipes, we are informed that the oil leaks have been reduced to less than 20 in 2007, with none of the leaks coming from pipe coated with the glass flake hybrid. One hundred and forty thousand linear feet of 4” road crossing pipe has been coated and 10,000 feet of 6”-36” pipe. Production has increased significantly due to the major reduction in down time and middle of the night call outs are almost a thing of the past. As an unexpected bonus, most of the engineers involved with leakage program were no longer required but due to the program’s success they have all moved onto bigger and better jobs within the customers organization.

Other fields are now taking advantage of the specialist coatings, application knowledge and service provided by our company. Also work expands into other areas such as the internal coating of waste brine pipes and the corrosion protection of gate and check valves at three central gathering stations.

Further, due to our tremendous success in giving corrosion protection in areas previously thought almost impossible, local operations of major American oil service companies, have taken advantage of our presence to coat frac acid tankers, waste treatment tanks and other ancillary oilfield equipment.

There are many glass flake coatings in the market these days but few of them have the research and background of those produced by us. Glass flake coatings properly formulated not only give outstanding performance but also long life cycles. Whole life costs can be very low indeed. Many of the advantages in using glass flake, such as fire retardancy and mechanical properties have been ignored and there is still a lot of work to
be done before all the benefits of glass flake pigments and the coatings produced from them are understood. They are however, very useful in the oil industry and much more useful than you might think!

CONCLUSION

Ongoing research and development into heavy duty ant-corrosive glass flake coatings continues to yield improvements. This work is time consuming and expensive but the knowledge and improvements gleaned, allow coatings to work in some of the more difficult environments at higher temperatures. This reduces down time, maintenance costs and in some instances negates the need for expensive metallurgy, which in its own right, is not always successful. In several industrial sectors including oil production and processing there are already proven areas of application and several other areas that could benefit from this advanced technology.

REFERENCES


