Silexine

Restoring the whiteness
in pinked PVC-u

WHITIN®

CONTENTS

“pinking is a wide-spread phenomenon in Europe and North America”

THE PINKING PHENOMENON

History of pinking

Pinking is a special, but widespread discolouration of PVC-u. It produces a characteristic light brown-pink colour sometimes called “mushroom shade” which deepens in colour with time. PVC-u can suffer from other discolourations such as yellowing, greying and chalking. Of these, only “yellowing” has been confused with pinking as “yellowing” can exhibit many colour shades, including pink.

Pinking has been experienced in Europe and North America for many years. Whilst becoming more prominent during the late 1980's it has, since the early 1990's become a major issue widely seen in PVC-u window profiles and foam boards.

Pinking is the result of a combination of specific titanium dioxide pigment properties with generic lead-based stabilisation used by extrusion manufacturers during this period. Extrusion manufacturers changed to non-pinking formulations in the late 1990's but only after many thousands of tons of potentially pinking PVC-u had been installed in the European and North American markets.

Pinking mechanism

For pinking to occur, both indirect sunlight and surface moisture are required. Pinking occurs predominantly in areas of high moisture such as coastal and hilly areas, and it also occurs more frequently on the North-facing sides of properties (indirect sunlight side) in Europe and North America. It has been found that pinking requires about 1.5 to 2 years (inductive period) before it starts to become apparent to the householder. The pink compound producing the pink effect is a chemical species of lead, which is produced by a reaction between the lead stabiliser, water, UV radiation and the titanium dioxide pigment. This lead compound producing the pinking effect is located in a thin layer near the surface of the pink PVC-u. Pinking can be reversed back to white by removing the PVC-u from a wet environment. It will re-occur by returning the PVC-u to the wet environment but without the 1.5 to 2 year inductive period being required. Exposure to direct sunlight can speed up the reversal of the pinking effect.

Pinking on buildings

Products such as window frames with mixed recipes of PVC-u on different sections can highlight pinking earlier than a product produced from the same (pinking) PVC-u. Skinned foam-filled PVC-u used for soffits and barge boards often exhibits stronger pinking than solid rigid profiles used for windows and doors, probably due to its thermal properties allowing them to retain a surface moisture layer longer than solid PVC-u. Effects on UV and water exposure due to shadowing by overhangs can result in large differences in pink colour strengths under eves and window openers.

Existing remedial options

- **Total replacement of affected products**
- **Spray coating affected components**
- **Chemical solvation of discoloured PVC-u followed by post-treatment neutralisation**

ALL THESE METHODS CAN BE COSTLY AND DISRUPTIVE

THE NEW WHITIN® PROCESS

Product development

Whitin® has been developed by Winnats Enterprises Limited (Dr. RH West and Mrs LH West).

Winnats personnel have over 25 years' experience in materials and surface chemistry. More specifically, for the past 10 years Dr West has been involved in the surface characterisation of pinked PVC-u and has built up considerable expertise in the subject including a theory for pinking itself and has translated this understanding into the development of a remedial treatment for the pinking process.

Working from this experience, a number of possible chemical reversal systems were investigated. Laboratory development of the final formulation, which subsequently became known as Whitin®, involved the following activities:

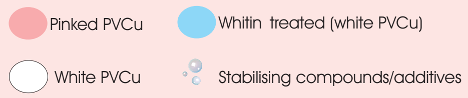
- ➜ Selection and sourcing of raw material samples.
- ➜ Compatibility, solubility, stability and efficacy testing of a large matrix of possible formulations.
- ➜ Optimisation of the application method.
- ➜ Preparation and monitoring of the natural weathering of treated PVC-u samples.
- ➜ Analysis of treated PVC-u samples.

Whitin® one-stage treatment to reverse pinking in PVC-u

- ➜ A one-stage chemical process offering:
  - Reversal of the pinking process in one operation.
  - Protection against subsequent pinking.
- ➜ The process can be less expensive than existing remedial alternatives.
- ➜ The treatment is weather-tolerant and can be applied any time of year.
- ➜ Treatment is easy to apply and environmentally friendly.
- ➜ Chemicals used are no more hazardous than many available to the DIY market.
- ➜ No elaborate safety measures required.
- ➜ No special protective clothing required, standard protective clothing is sufficient.
- ➜ No masking off of adjacent areas necessary.
- ➜ Evacuation of premises not required during treatment.
- ➜ Whitin® is applied through a national network of applicators.
- ➜ Whitin® applicators are fully trained and individually licensed.
- ➜ A guarantee is offered with every treatment.

PRINCIPLES OF ACTION

Whitin® is a new chemical treatment for pinked PVC-u, in which the secondary (weak) bonds of the resin matrix are broken temporarily to allow penetration of an activator to reverse the pinking reaction, together with additives to provide stability against future weathering processes (see diagrams 1-4).



BEFORE TREATMENT

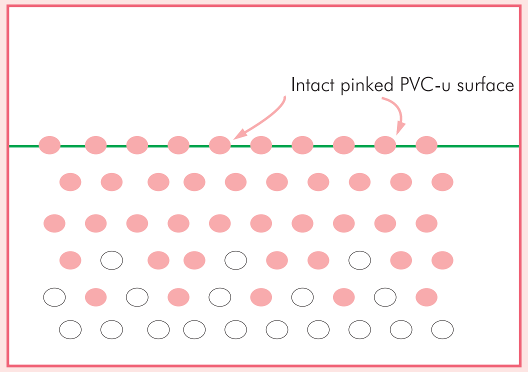


DIAGRAM 1

JUST AFTER TREATMENT

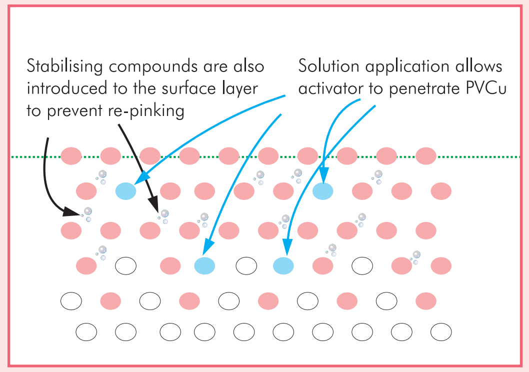


DIAGRAM 2

1 HOUR AFTER TREATMENT

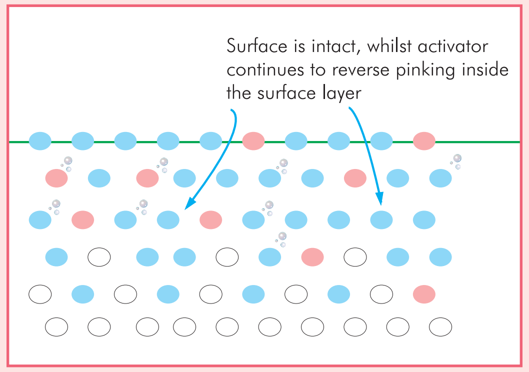


DIAGRAM 3

24 HOURS AFTER TREATMENT

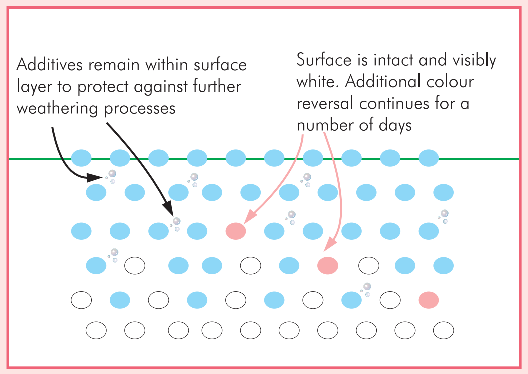


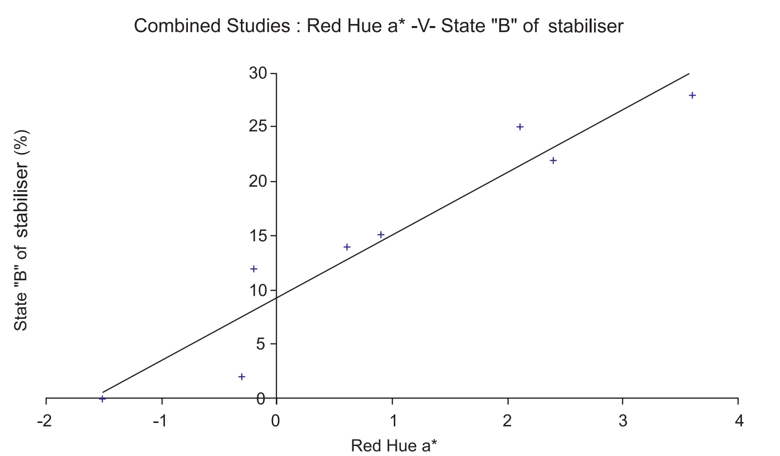
DIAGRAM 4

WHITIN® RESEARCH AND DEVELOPMENT

Long term stability of Whitin® treated PVC-u

In March 2001, a paper on PVC-u discolourations was published by Isabelle Georges-Guerand, Research and Development Engineer at Solvay-Benvic Ltd (Ref. 1). She studied pinking discolouration, and concluded “The photoactivity of titanium dioxide has been clearly demonstrated as being a main parameter influencing pinking. For a given family of stabilisation, whatever the stabiliser, the occurrence and the intensity of pinking is directly related to the photoactivity of TiO_2 (the higher the photoactivity, the sooner and the more intense the pink coloration). Concerning the other parameters (fillers, impact modifiers, type of resin), no significant influence has been established.”

Fig. 1 (Ref. 1)



X-ray photoelectron analyses of pink material from the surface of pinked PVC-u samples, in comparison with similar material from non-pinked samples was shown to exhibit spectral peaks characteristic of both the Pb[+II] and Pb[+IV] states. Non-pinked material showed only Pb[+II] peaks. It was also observed that the intensity of the Pb[+IV] peaks (described in ref. 1 as ‘State B’) could be related linearly to the Red Hue (a*) colour parameter. (Fig. 1)

The explanation offered for this observation was: “The normal state of lead in a profile with this kind of stabilisation is Pb[+II] (from PbO, or $PbCl_2$ when the stabiliser is consumed). In the case of pinked samples, a part of Pb[+II] has been oxidised into Pb[+IV]. As the photoactivity of titanium dioxide has been demonstrated to be the main influence in the pinking phenomenon, It is assumed that the titanium dioxide interacts with the stabiliser to oxidise it.” Pinking is observed to require moisture and indirect solar (UV) radiation in order for the process to occur. Removal of the PVC-u from such an environment causes the reversal of the pinking discolouration; subsequently returning a sample to the environment triggers pinking again.

References

1) Turning the light on unusual colorations of PVC profiles; I. Georges-Guerand; Profiles 2001.

Treatment with Whitin®

When the pinked PVC-u surface is treated with Whitin®, a number of additives are carried into the PVC-u surface and then locked into the matrix.

Chemicals are included in Whitin® that perform the following actions:

➜ Reverse and lock the lead chemistry so that Pb[+IV] disappears permanently.

➜ Provide protection against ingress of moisture to the system.

➜ Include additional stabilisation to remove any organic free-radicals which could be associated with the creation of Pb[+IV] ions.

➜ Ultra-violet absorbers are also incorporated to (doubly) protect against the formation of Pb[+IV] ions and against damage to the PVC-u polymer chains.

The above components are trapped within the PVC-u, near the surface.

Evaluation of the Georges-Guerand Pinking Index and CIE L*a*b* Colour Parameters for PVC-u Profile Samples Treated with a Prototype Surface Modification Formulation

Pinking Index

A pinking index “PI” was defined in a paper entitled “Turning the light on unusual colorations of PVC-u profiles” presented by Isabelle Georges-Guerand, of Solvay-Benvic at “Profiles 2001” conference in March 2001 (Ref. 1).

The Georges-Guerand pinking index is defined as follows: PI = {(a* + b*/2)/100} L*

Where a*, b* and L* are the CIE colour parameters measured from the PVC-u surface. The higher the pink index PI, the more intense the pink coloration.

The trend in pinking index PI for two prototype surface modification treatments of profile samples over one year of exposure in an extreme pinking environment is presented in Fig. 2 and the variation in the CIE colour parameters in Figs. 3-5:

Fig. 2

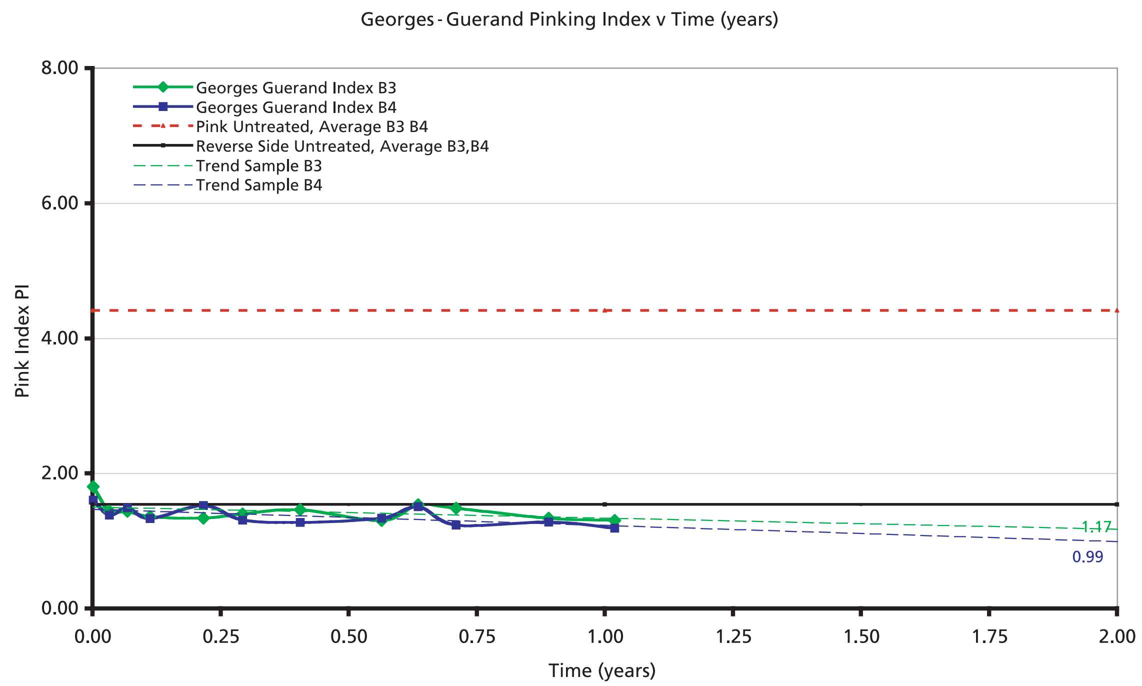


Fig. 3 Red / Green Parameter a*

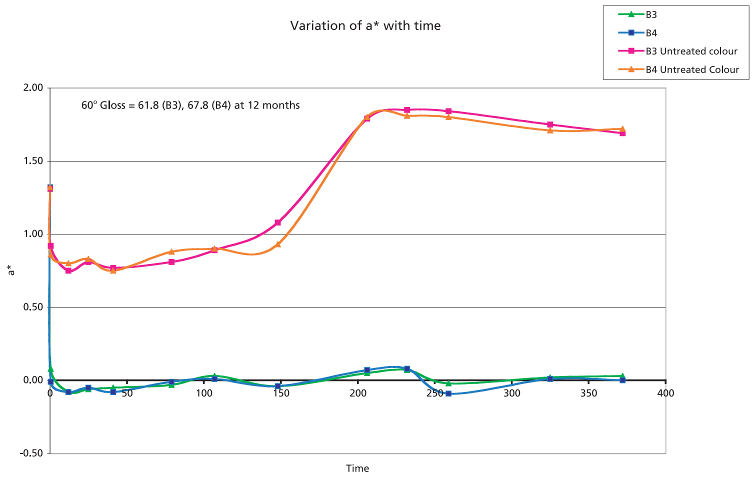


Fig. 4 White / Black Parameter L*

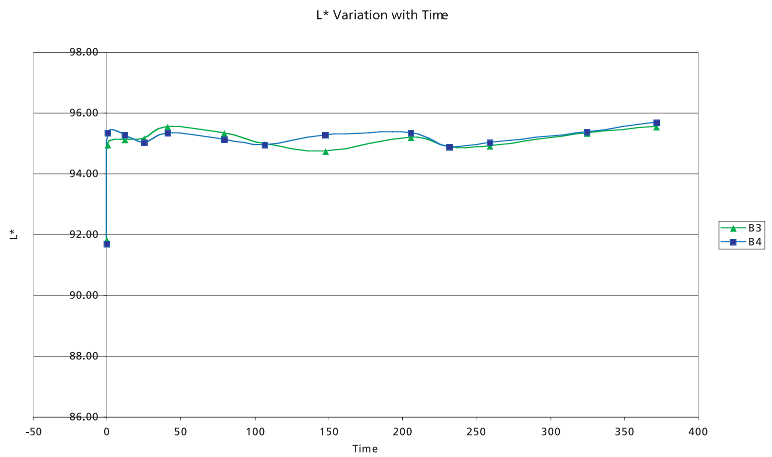
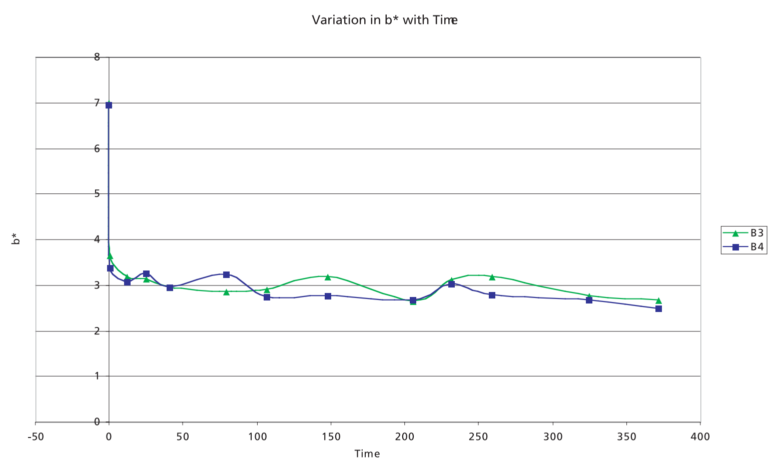


Fig. 5 Blue / Yellow Parameter b*



CIE L*a*b* Colour Parameters

Figures 3-5 show the variation in the CIE L*, a* and b* colour parameters over one year for the above samples. Before treatment, both samples showed decreased L* and increased a* and b* parameters compared to the range of values specified for new PVC-u. After treatment the colour parameters of both samples returned to the 'as new' range, whilst untreated areas of the samples were observed to remain discoloured (as shown by the upper curves in figure 3).

Conclusions

During the first year of weathering, the treated areas of both samples have remained the same colour or slightly whiter than the unexposed (white) reverse side of the same PVC-u profile. To the naked eye, they have the same level of whiteness as the white unexposed side of the PVC-u profile.

No indication of any return of pinking discolouration is observed in the first year of exposure.

CIE L* a* and b* colour parameters all remain within a range acceptable for new PVC-u during the year that the treated samples have been exposed for weathering.

XRF SAMPLE ANALYSIS

Analysis of Treated and Untreated PVC-u by XRF

Whitin® includes additives that contain specific chemicals. One of these contains at least one element that is known not to be present in lead stabilised PVC-u, so it can be used as a chemical marker for the presence of Whitin® treatment on lead stabilised PVC-u.

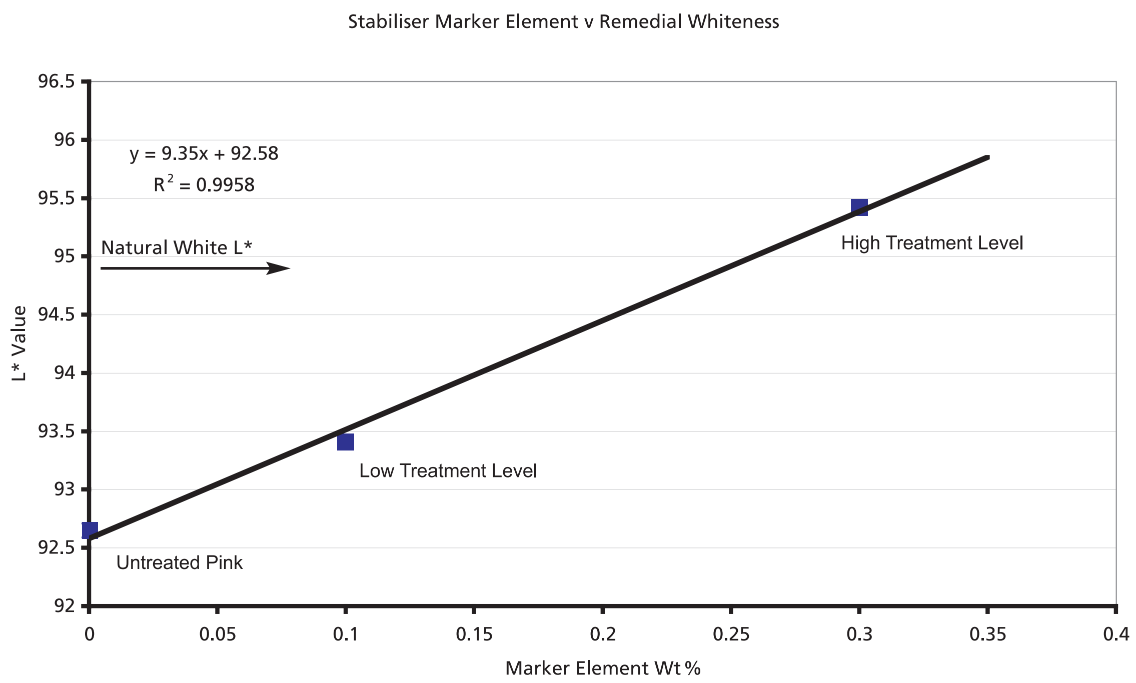
Elements from sodium upwards can be analysed by X-ray Resonance Fluorescence (XRF) and the quantities of these elements can be determined relatively accurately. So, detection of the marker element(s) in PVC-u would confirm that Whitin® had been applied and the amount present would indicate the amount of Whitin® fluid that had been absorbed at any place on the PVC-u.

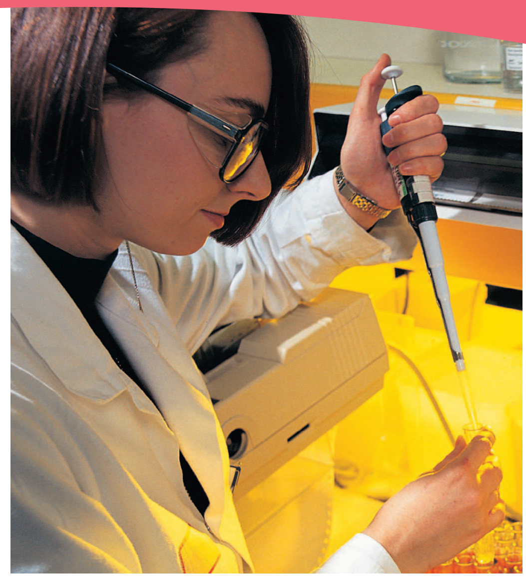
XRF analysis was undertaken on a piece of lead stabilised PVC-u which had been partly treated with Whitin® at two different levels so that three areas existed for XRF: (1) pink (2) near white and (3) pure white. The colour parameters of the three areas were also measured for comparison with the XRF results. (Fig. 6)

Semi-Quantitative XRF Analysis (Qual-Quant)

The three areas of interest on the PVC-u plaque were located using the observation camera fitted to the XRF instrument. Semi-quantitative analysis was carried out for all elements from sodium to uranium using the fundamental parameters (FP) method. The balance of the material was assumed to be PVC-u (C_2H_3Cl). Although the coating was applied to the surface of the sample only, this was not taken into account when setting up the experiment. The sample was treated as bulk material.

Fig. 6





Colour Measurements

The colour parameters of the PVC-u plaque were analysed by a Minolta CM-503i spectrophotometer over the visible range from 400nm to 700nm. The L*, a*, b* values for the three exposed areas and fourth unexposed area on the PVC-u plaque are listed in Table 1.

Colour Parameter Values

Table 1

History	L*	a*	b*
Exposed / Untreated	92.65	1.17	6.74
Exposed / Low Treatment	93.41	0.25	4.76
Exposed / High Treatment	95.42	0.05	3.04
Unexposed / Untreated	94.81	0.21	3.03

Marker element concentration (XRF) and L*,a*,b* colour parameters indicate the amount of Whitin® applied to the PVC-u listed and so both methods can be used as indicators for the effectiveness of Whitin® treatment applied.

Each of the colour parameters (table 1) are plotted against marker element concentrations in Figs. 6-8. These plots measure the relative cause and effect of Whitin® on the different colour parameters of the PVC-u. The "natural white" values in these plots are the L*,a*,b* readings from the unexposed areas of the profiles.

Fig. 7

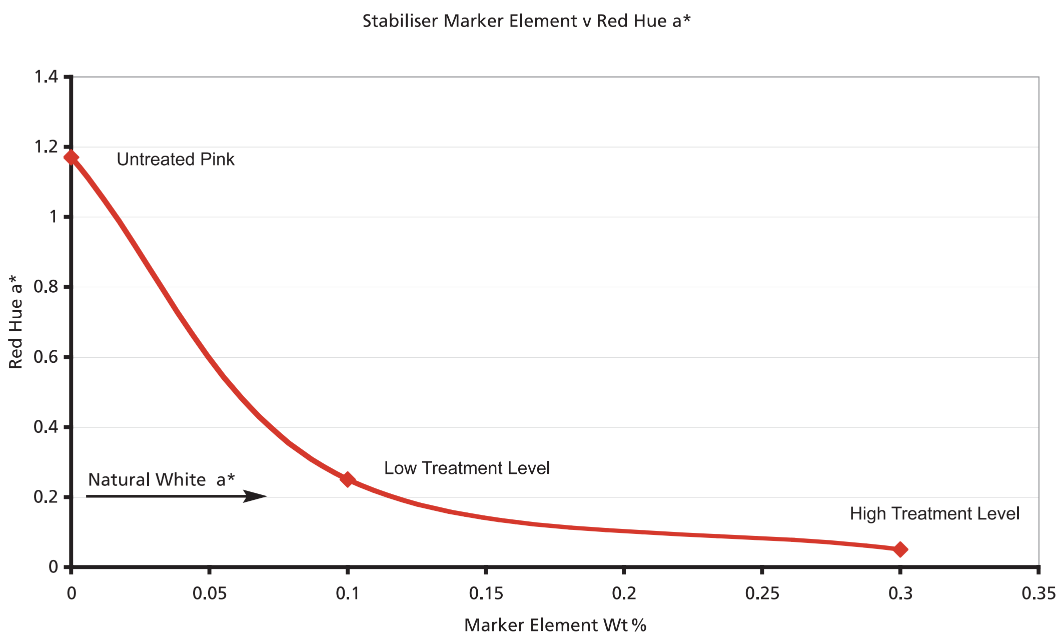
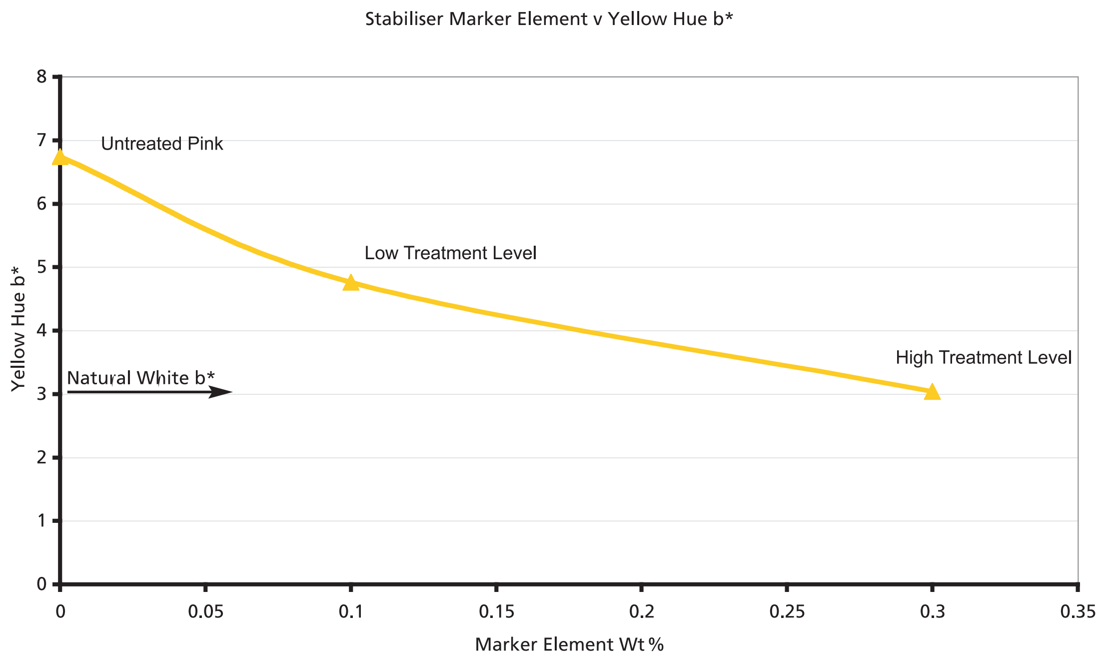


Fig. 8



Observations

➜ There is a linear increase in the white parameter L* with increasing marker element (and hence Whitin®) concentration.

➜ There are non-linear decreases in the red a* and yellow b* colour parameters with increasing marker element (and hence Whitin®) concentration.

➜ A Whitin® treatment produces the appropriate reversal of colour without inducing any physical modification of the PVC-u surface.

These results imply that the efficiency of Whitin® application by any applicator can be monitored and quantified from the L*, a*, b* colour measurements made over time on site, and then applying this data to the calibration plots such as Figs. 6-8. Both under and over treatment levels can be detected by this post-analysis.

Conclusions

The following conclusions can be drawn from the technical development of Whitin®.

➜ The active ingredient of Whitin® reverses the chemical state of the "pink" compound of pinked PVC-u.

➜ Solvents have been selected to allow the active ingredient to access the "pink" compound within the appropriate depth of PVC-u pinking.

➜ A package of additives is included which modify the composition of the former pink layer on PVC-u so that the pinking process is inhibited from returning even in the most extreme (pinking) climates.

➜ The application of Whitin® treatment can be monitored and confirmed by colour and gloss measurements and also by chemical analysis using XRF.

CASE STUDY

Product development

Trial site A: This area was a continuous run of six double frames and adjoining (LH) single frame.

PVC-u Evaluation

Prior to application of Whitin®, the window frame was evaluated for colour and gloss parameters. Colour measurements were made with a Minolta 503i spectrophotometer, and gloss measurements at 60^{o} with an Elcometer Tri-Gloss meter after the pre-wash had been completed, but prior to treatment commencement.

Post Treatment Colour / Gloss Measurements

Once the surface was touch-dry (approximately twenty minutes after treatment was complete) colour and gloss measurements were taken from the same areas as before.

Table 2: Colour and Gloss Measurements Prior to Whitin® Treatment

Locations	60° Gloss	L*	a*	b*
1) RHS of LH Frame	49.2	92.12	0.90	5.38
2) Upright (Low Pinking Level)	33.0	93.71	-0.12	2.66
3) Centre Bar of Frame 1	59.3	91.16	0.94	5.78
4) Centre Bar of Frame 2	61.5	91.45	0.87	5.47
5) Centre Bar of Frame 3	60.0	90.49	0.90	5.75
6) Centre Bar of Frame 4	60.8	90.99	1.00	5.80
7) Centre Bar of Frame 5	62.7	90.14	1.05	6.18
8) Centre Bar of Frame 6	62.5	89.45	1.05	6.27
9) Centre Frame 2/3 Vertical		91.41	0.54	4.88
10) Sill at Frames 1/2		88.39	1.38	8.92
11) Sill at Frames 4/5		88.78	1.31	7.98

Table 3: Colour and Gloss Measurements after Treatment with Whitin®

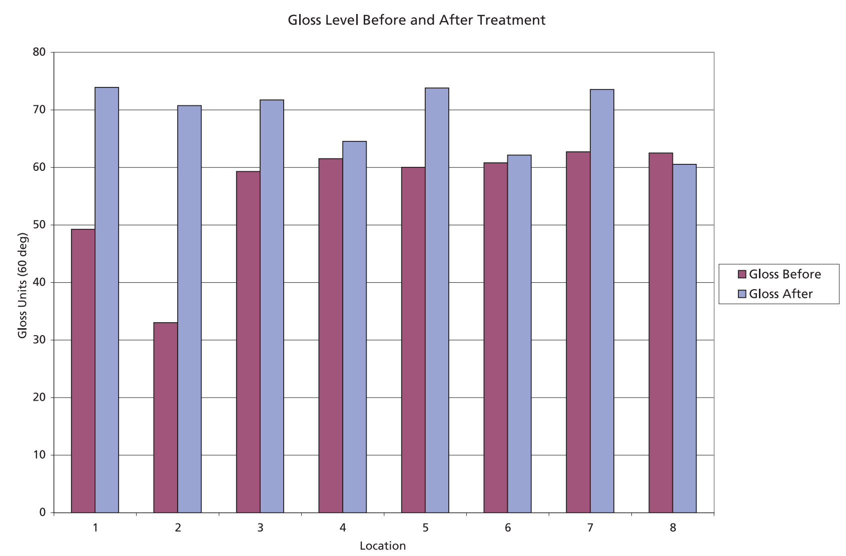
Locations	60° Gloss	L*	a*	b*
1) RHS of LH Frame	73.9	95.45	0.12	3.15
2) Upright (Low Pinking Level)	70.7	95.12	-0.22	1.65
3) Centre Bar of Frame 1	71.7	94.80	0.34	3.67
4) Centre Bar of Frame 2	64.5	92.99	0.44	4.17
5) Centre Bar of Frame 3	73.8	94.25	0.29	3.63
6) Centre Bar of Frame 4	62.1	92.02	0.64	4.83
7) Centre Bar of Frame 5	73.5	93.65	0.39	4.20
8) Centre Bar of Frame 6	60.5	93.86	0.56	4.38
9) Centre Frame 2/3 Vertical		94.47	0.16	3.23
10) Sill at Frames 1/2		93.48	0.26	4.08
11) Sill at Frames 4/5		92.70	0.23	4.00

Comparison of the gloss and colour parameters before and after Whitin® treatment (values from Table 2 and 3) is presented in Figs. 9-12 thus:

There is a general increase in gloss on treatment with Whitin® as shown in Fig. 9. The increase in gloss could be measured less than one hour after treatment. The gloss in Location 2 has more than doubled and would give the appearance of "new PVC-u".

Generally, the gloss levels are much more uniform after Whitin® treatment (60 – 74 units at 60^{o}).

Fig. 9

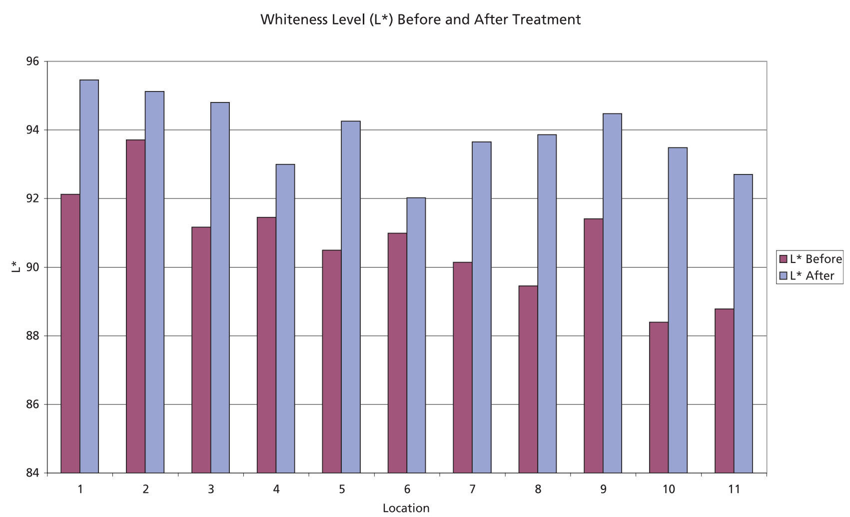


Colour L* (Black – White) Values

There is a general increase in whiteness in all areas treated by Whitin®.

The general trend, from higher to lower L* values from left to right, is due to the difference in time after treatment before measurement is made.

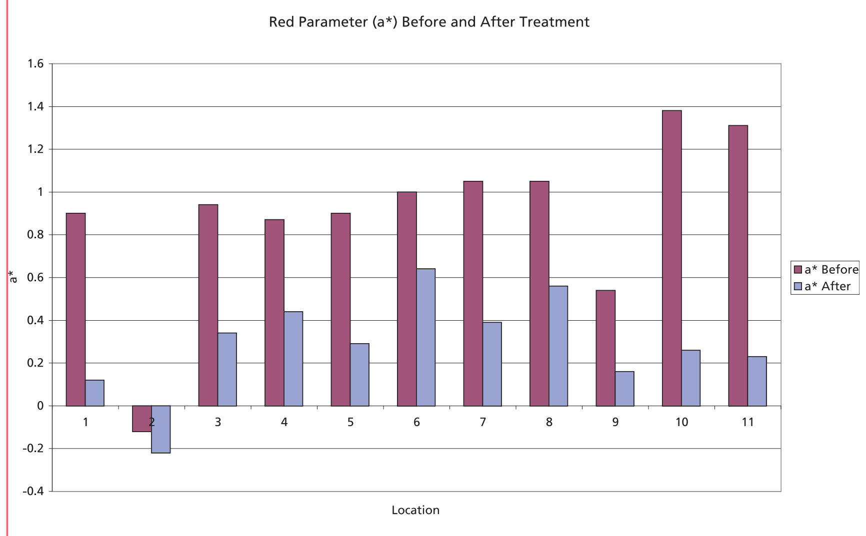
Fig. 10



Colour Red a* Parameter Values

Red parameter values are reduced in all areas treated. The rate of red reduction per hour will depend on several factors such as the penetration rate of the PVC-u by the solvents and active ingredients. Overall the range of a* values after treatment will be smaller than the range before treatment.

Fig. 11

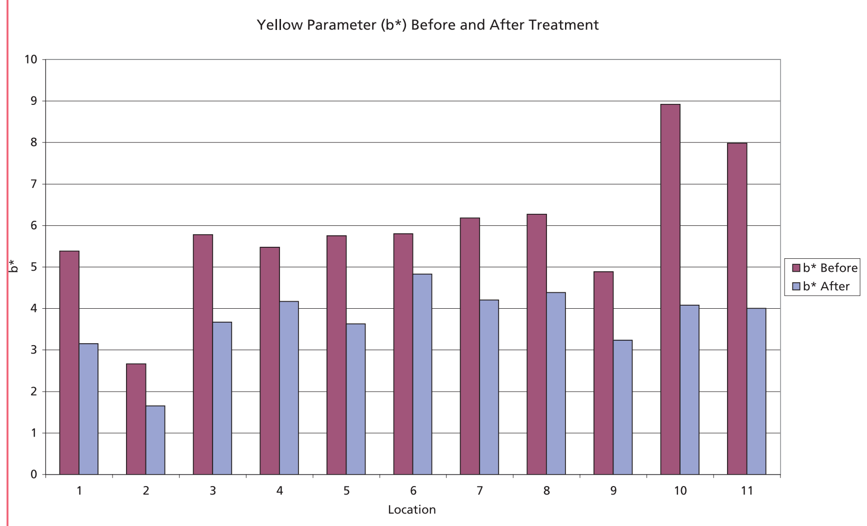


Colour Yellow b* Parameter Values

In Figure 12, the yellow parameter b* values for 8 of the 11 locations are up to 50% lower than the untreated values less than one hour after treatment.

Differential pinking effects were visually reduced or removed within one hour of treatment.

Fig. 12



WHITIN® APPLICATION SYSTEM

Silexine Coatings Limited

Silexine Coatings Ltd is an associated company of Biokil Crown Ltd, an independent, privately owned British company, which has grown to become one of the U.K.'s largest manufacturers and suppliers to the Building and Construction Industry of Damproofing Chemicals, Timber Preservatives and Waterproofing Products. Biokil Crown also supplies Adhesives, Sealants and general building chemicals.

Biokil Crown's comprehensive training and support for products is provided nationwide by a team of fully trained Sales & Technical Consultants and is further supplemented by in-house training facilities and by an on-site Technical Specification service.

National Network of Approved Applicators

Biokil Crown Ltd manufactures Whitin® for Silexine Coatings Ltd. Biokil Crown has a network of over 600 Approved Contractors throughout the United Kingdom, fully trained in remedial treatments. Silexine has utilised this expertise and selected over 50 Approved Contractors with a geographical coverage of the U.K. and Eire ready to provide a cost-effective solution to pinking, all having been fully trained in the application of Whitin®.

Training

The Silexine training team is headed by Howard Goslyn AIWSc FinstRTs MEWI, who specialises in the training of remedial surveyors and technicians for certification in the building industry (BWPDA/CITB).

Each individual trainee, upon successful completion of the course, is certificated and allocated a specific Whitin® Applicator Reference number. This Reference number is inserted on individual application contract forms so that each job can be tracked back to the individual operative/employee of an Applicator Company. Certification will be removed in the event of misconduct or poor work.

In order to ensure that treatments are being carried out to the correct specification, Silexine makes random spot checks and testing.

Guarantee

The Silexine management team has experience in the provision of industry guarantees spanning 30 years. This includes the expertise to cross correlate materials purchased, against material usage per contract, thus monitoring overall standards.

When the Whitin® application has been completed and a Satisfaction Note, signed by the householder is received, a guarantee is offered on the product and application of the process.

Silexine believes that the Whitin® system provides the total answer to the pinking problem.

From manufacture to application our aim is a satisfied customer with white profiles.

CONTACT

To find out more about the Whitin® process system contact:

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