Dr Juan Zhou, Zhiqun Ye, Dr Joshua Taylor, Dr Rachel Sun, Dr Leo Fan, Cyfer Chen and Dr Satish Gaonkar, BASF, discuss how their latest low odour, dispersion-formulated paints perform

against some of the premium interior products in the market

Novel dispersion for near zero VOC/ low odour premium interior paints with outstanding stain resistance property

ASF strives to develop cutting edge technologies to deliver near-zero VOC solutions to produce more environmentally friendly coatings. In this article, we will demonstrate how BASF's new third generation low odour dispersion Acronal ECO 7653 formulated paints perform against some of the premium interior products in the market. This article will explain the popular standards and labelling on VOC regulations used for paints in different countries. It will also give details on paint formulation know-how to achieve near-zero VOC and low odour using Acronal ECO 7653 dispersion. It is proven that a near-zero VOC low odour paint with superior stain resistance can be achieved without compromising important functional properties, such as TVOC, freeze thaw stability and burnish resistance.

Table 1. Formulation of 40% and 50% PVC of near zero VOC low odour paint using Acronal ECO 7653

INTRODUCTION

The increasingly demanding environmental regulations have put enormous pressure on

RM	Dosage (g) PVC 40%	Dosage (g) PVC 50%	Notes	Supplier				
Water	177.0	197.0	Deionised	-				
Dispex AA 4140	4.5	4.5	Dispersant	BASF				
Dispex CX 4320	2.4	2.4	Disperant	BASF				
Dispex Untra FA 4480	1.5	1.5	Wetting agent	BASF				
Foamaster NXZ	2.0	2.0	Defoamer	BASF				
Natrosol 250HBR	2.5	2.5	Thickener	Ashland				
Silquest BS 16	2.0	2.0	pH adjustor	Wacker				
Tipurew R-706	210.0	210.0	TiO ₂	DuPont				
Omaycarb 2	110	115.5	CaCO ₃	Omya				
DB-80	60	84	Cal KaoLin	Jin Yang				
Let down								
Loxanol 5290	17.3	13.2	Coalescent	BASF				
Acronal ECO7653	375.7	284.9	Dispersion	BASF				
Strodex FT68	4	3	Anti-freezer	Ashland				
Foamaster A10	2	2	Defoamer	BASF				
Acticide MV	1	1	In-can biocide	Thor				
Acticide EPW	3	3	Dry film biocide	Thor				
Rheovis HS 1212	4.5	4.5	Thickener	BASF				
Water	20.6	67.0	Deionised					
SUM	1000	1000						

the coating industries to develop products that cause less impact to the environment. With rapid economic growth, frequency of painting and repainting has been increasing in most of the Asian countries, such as China and India and hence, end-users now raise more concerns on paint safety and functionality to ensure their household / interior is safe and healthy. Public awareness of indoor air quality has played a major role in introducing the concept of low Volatile Organic Compound (VOC)¹ paints in some of the Asian markets. Architects and construction professionals also consider durability of a paint to be of the utmost importance. High durability will, theoretically, lead to a decrease in the need for repainting, resulting in less carbon footprint. Paint manufacturers across the globe have successfully launched some eco-friendly products²⁻⁴, such as low VOC and low odour paints to address the market needs. However, technologies of application properties in eco-friendly paints are not satisfactory, especially stain resistance. This is mainly caused by formulation changes made for achieving low VOC and low odour.

To pursue a 'Clean Air' concept in its products, BASF is committed to bringing high performance low-VOC low-odour products to customers. It applies a variety of purification technologies, such as physical deodorisation and chemical treatment, to remove the odour and VOC of its dispersions. This enables paint industries to formulate their coating formulation with a 'cleaner/purer' dispersion, as well as with enhanced application properties.

This paper will explain how BASF Acronal ECO 7653, the third generation low odour solution fulfils near-zero VOC/low odour criteria with excellent stain resistance and other important application properties. We should note that, 'low VOC' and 'zero-VOC' paints are not the same – for instance, the current GB18582-2008 standard in China for a 'low VOC' paint means the TVOC level needs to be less than 120g/lit; whereas 'zero-VOC' paints have to be less than 20g/lit according to a Chinese standard JG/T 481-2015.

FORMULATION

The binder used in this work was a styrene acrylic polymer using BASF latest Acronal ECO

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Country	Scheme	System	VOC limit	Units	Comments
China	GB 18582-2008	Interior	<120	g/lit	Water excluded
	JG/T 481-2015		<20	g/lit	Near zero VOC
	А		<3.0	mg/m³	After 72hr
	A+		<1.0	mg/m³	After 72hr
Australia	The Australian Ecolabel Program	Interior	16	g/lit	Low sheen, semi-gloss, flat washable
New Zealand	The New Zealand Ecolabelling Trust	Interior	55	g/lit	Flat washable
Philippines	Green Choice Philippines	Interior flat	50	g/lit	GCP-2007013 water- based paint
Malaysia	Eco labelling scheme	Emulsion	50	g/lit	
Singapore	Eco labelling scheme	Interior	25	g/lit	Matte
Thailand	Eco labelling scheme	Water slurry and emulsion	50	g/lit	Matte
India	Green Seal GS-11	Flat top coat	50	g/lit	Water excluded. Most paint companies follow this guideline

Table 2. Dispersion, paint and paint emission VOC limits (interior) from different countries

7653 dispersion, with a minimum film formation temperature (MFFT) of 25°C. The solid content was approximately 45-47% and pH value was between 7 and 9. Table **1** provides the guiding formulation of 40% and 50% PVC of near-zero VOC low odour paint. The PVC of these market benchmark paints was between 40% and 50% based on the rough calculation of their ash and solid contents. The formulations were designed carefully by using formulation additives that would not add any additional VOC at the same time, which also assured the performance of paint properties, such as stability and excellent film formation.

BENCHMARKS

All the paint properties of Acronal ECO 7653 were compared to three selected market benchmarks in low-VOC, low-odour category. Benchmark 1 and Benchmark 2 claimed to be a low-VOC/low-odour product. The reason for choosing Benchmark 2 was for its excellent stain resistance performance,

which was claimed to be one of the best in China market. Benchmark 3 was a premium near Zero-VOC product specialised for children's bedrooms, playgrounds, nurseries, kindergartens etc.

RESULTS AND DISCUSSIONS (1) TVOC (Total Volatile **Organic Compound)**

Green labelling is a global marketing trend recognised by consumers as signalling improved environmental sustainability. The Global ECO Labelling Network⁸ is an association of organisations worldwide that develop and promote sustainable ECO labelling practices. Governance regarding Interior Paints VOCs is built around maximum allowable concentrations in the polymer dispersions, maximum allowable concentrations in the paints (by segmentation) and maximum allowable limits regarding the emitted VOCs under given conditions. Examples for different countries are summarised in Table 2. It

is observed that different APAC countries follow different guidelines. As the public is more concerned about indoor air quality (IAQ) nowadays, the VOC limit has become much lower compared to what the level set some years ago. Some countries like India may not have strict domestic regulations but paint manufacturers still urge for eco-friendly products for healthier living environments.

BASF's new Acronal ECO 7653 is a third generation low-odour dispersion that possesses near-zero VOC and low odour features with excellent stain resistance and very good film forming properties. The formulation latitude of Acronal ECO 7653 helps provide an outstanding balance between storage stability and performance at various PVC levels.

Total VOC (TVOC) levels were tested by using BASF internal methodology developed for paints based on the GC method. Figure 1 shows TVOC data of three market benchmark paints and paints formulated with Acronal ECO 7653. The results are consistent concerning both C14 and C16 required criteria.

Among the three market paints, Benchmark 1 performs the best with its TVOC more than 2q/lit. Benchmark 2 claimed to be a low-VOC paint with excellent stain resistance performance. However, the results show that its TVOC level is as high as 42.35g/lit with C14 and 56.83g/lit with C16, which indicates that Benchmark 2 does not possess the technology to accommodate both low VOC level and stain resistance property. The paint with Acronal ECO 7653 outperforms the others by less than one order of magnitude in both formulations - 0.45g/ lit TVOC with C14 at 40% PVC, 0.27g/lit TVOC with C14 at 50% PVC and, 0.78g/ lit with C14 at 40% PVC, 0.48g/lit with C16 at 50% PVC. As the TVOC results of C16, which is equivalent to a boiling point of 280°C, are at a very low level, therefore, Acronal ECO 7653 formulated paints can definitely be considered as 'near-zero VOC'. BASF's Acronal ECO 7653 can

Figure 1. TVOC comparison of Acronal ECO 7653 formulated paints and three market benchmarks

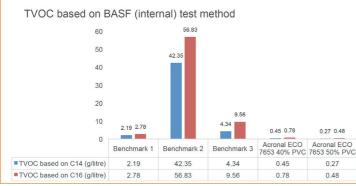




Figure 2. Odour sniffing in progress

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Figure 3. Odour panel tests results of BASF's Acronal ECO 7653 related paints and three market benchmark paints

comfortably comply with the Australian Ecolabel Program, which has the most stringent limit – TVOC lower than 16g/lit; as well as the China JG/T 481-2015 nearzero VOC standard <20g/lit. The Acronal ECO 7653 formulated paints can easily satisfy low/near-zero VOC standard without compromising stain resistance (results are shown in **Figure 3**).

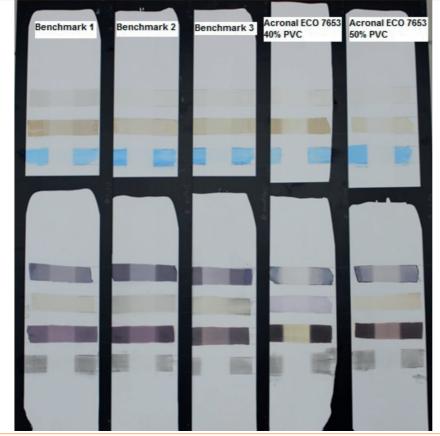
Volatile matter emitted from paint is a commonly-known contaminant that causes different problems in some clean-room environments. Achieving near-zero VOC in paints would enable end-users to apply this for hospitals, pharmaceutical and food industries, kindergartens etc, wherever clean air is desirable.

(2) Odour

Odour is one of the most argued issues as the test method for odour analysis is very subjective. In order to obtain the highest quality results, 10 panellists were hired to perform the odour sniffing test. Hedonic scale 5,6,7 was adopted for the panellists to rank their perception of odour – 1 was 'like extremely' and 5 was 'dislike extremely'. **Figure 2** shows how our panellists evaluate and test the odour of our selected products.

Figure 3 shows that the paints using Acronal ECO 7653 have the lowest possible odour level as panellists gave the best rating. It is known that a low VOC product does not necessarily mean low

Figure 5. Stain resistance panel after 200 washing cycles. From top to bottom: vinegar, black tea, blue crayon, blue black ink, water soluble nigrosine, alcohol soluble nigrosine, Vaseline black



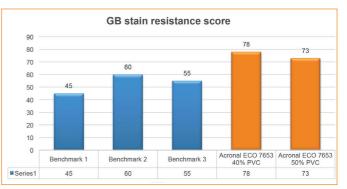


Figure 4. Stain resistance comparisons

odour, however, the Acronal ECO 7653 formulated paints clearly show that low TVOC significantly lowered the odour level ranking, giving a truly 'Clean Air' solution to paint manufacturers and end-users.

(3) Stain resistance

The sample was drawn on a Leneta black plastic panel with a film thickness of 150µm meters and then cured the panel at a controlled temperature and humidity room for seven days before testing. The test was done according to GB/T 9780-2013 standard – a test method for dirt pick up resistance and stain removal of film of architectural coatings and paints.

There were six types of stains, four of them were hydrophilic – vinegar, black tea, blue black ink, water soluble nigrosine, and two were hydrophobic stains: alcohol soluble nigrosine and Vaseline black. The assessment of stain resistance score was based on the measurement of reflective indices of the cured paint panel before applying those stains and after scrubbing the stains from the paint.

The China's GB stain resistance standard requires at least 60 points to pass premium Grade I. Figure 4 shows the Acronal ECO 7653 paint scores 78 (40% PVC) and 73 (50% PVC), which exceeds the GB standard and outperforms the three benchmarks. Furthermore, Figure 5 demonstrates that the Acronal ECO 7653 formulated paints deliver better performance in both hydrophilic stains and hydrophobic stains. Such outstanding performance can only be achieved by advanced technologies and precise formulations. It also confirms that the formulation latitude of this new dispersion was very good. The coalescing solvent Loxanol 5290 played a vital role in giving excellent film formation with providing good application properties.

(4) Burnish resistance

Burnish resistance is an important property to reflect how gloss or sheen of a coating film can be affected due to polishing or

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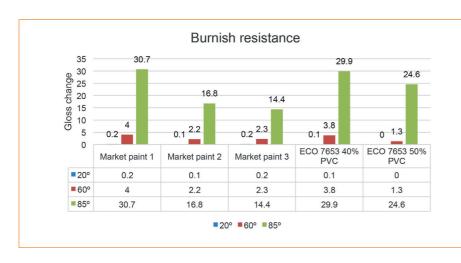


Figure 6. Burnish resistance (gloss change after rubbing) of paint films

rubbing. This was calculated by measuring gloss of the paint film before and after rubbing 200 wet scrub cycles. 20°, 60° and 85° were chosen for this test based on HGT4756-2014.

Figure 6 demonstrates that gloss changes of Acronal ECO 7653 at 20° and 60° are among the best compared to other benchmarks. In addition, according to HGT4756-2014, gloss change at 85° should be below 40 units if the gloss level at 60° is less than 10 units, which Acronal ECO 7653 formulated paints could meet without any issues.

(5) Freeze-thaw stability

Freeze thaw stability test was carried out at -5° with five cycles according to GB/T 9268-2008. All the tested samples passed this test. However, when TVOC measurement was carried out on the benchmark samples, low boiling point of solvents, eg Propylene/Ethylene glycol and Ester alcohol, were detected in some of these market paints. The use of approximately 3% anti-freezer Strodex-FT68 in our formulation helped increase freeze-thaw stability of the paint. This anti-freezer could adversely affect other application properties. Having said that, it did not apply to Acronal ECO 7653 related paints as the formulations were carefully designed.

(6) Wet Scrub Resistance

Wet scrub resistance was tested using GB/T 9756-2009 standard. All the samples passed more than 10,000 cycles, which is much more than what GB standard requires – passing 5000 cycles for premium grade paint. **Figure 7** demonstrates GB scrub resistance panels of Acronal ECO 7653 related paints and Benchmark 2, which could also offer good wet scrub resistance based on numerous scrub tests we have run.

(7) Storage stability

The prototype was stored in a 55°C oven for two weeks and the increase of viscosity was less than 10KU compared to initial viscosity. As benchmarks were commercial paints, we were not able to acquire the initial viscosity data for comparison. Therefore, we would assume that they have achieved required storage stability.

CONCLUSIONS

Some technical challenges still need to be overcome to achieve excellent functional properties, considering the low-VOC targets posed by many existing and proposed regulations. Using latex polymers with lower glass transition temperatures is one of the options as it requires less coalescing solvents and lower VOC demands. However, this solution also leads to many other problems as other properties of these binders can be adversely affected. Nonetheless, paints with near-zero VOC and excellent functional properties can be developed by choosing right dispersion and vigorous formulation. With carefully calculated formulas and latest innovative technologies, waterborne latex coatings can reduce VOC levels significantly without comprising different application properties. Furthermore, the VOC level is much lower than using the traditional solvent borne technologies.

This article has demonstrated that a near-zero VOC low odour paint can be achieved without compromising important functional properties, such as stain and burnish resistance, storage and freeze thaw stability. Innovative dispersion technologies in chemistry from BASF are helping paint industries to overcome the long-time issue of poor stain resistance of low odour/zero VOC paints. The use of right additives in a paint formulation has given a synergetic effect in achieving desired results. This



Figure 7. GB scrub resistance of paint panels

technology will provide a great opportunity for customers to provide 'Clean Air' with improved indoor air quality, aesthetic and durability of their paints to end-users. Moreover, it will also help protect our environment and health – at home, in the office or anywhere indoors.

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