DECORATION VEHICLES WITH LOW ENVIRONMENTAL IMPACT

C. David Díez

Kerafrit, S.A.

Spain

1. INTRODUCTION

Given our company's profound concern for the environment and it having been awarded the Integrated Environmental Authorisation, the next question we asked was: Would it be possible to develop decoration vehicles with a low environmental impact? The challenge was given to the R&D+i department, who set to work to develop this new range of vehicles.

The main pollutant when formulating vehicles is the increase in Chemical Oxygen Demand (COD). Chemical oxygen demand measures the amount of oxygen consumed by the raw materials present in water and liable to oxidise under certain specific conditions. Indeed, the measurement is an estimation of the oxidisable matter, whether organic or mineral, present in the water. COD depends on the characteristics of the actual matter, its respective proportions, its susceptibility to oxidise, etc., so that clearly the results can be reproduced and interpreted satisfactorily provided that the work protocol employed is well defined and carried out with meticulous care.

To summarise this demanding but nevertheless determinant way of quantifying water pollution, COD is used as a way of measuring the degree of pollution in water and is expressed in mg O_2/l, so that the smaller the amount of organic pollutant present, the less oxygen is consumed, which is turn means a reduction in COD and therefore greater mitigation of global warming.

It should also be added that in recent years, environmental management in business has changed from a legal requisite that was often avoided to becoming an essential part of the business plan, mainly as a result of the degradation of our planet.

Another fact to bear in mind in this regard is that experts in environmental health and cardiologists of the University of Southern California have proven that environmental pollution in large metropolitan areas affects our cardiovascular health. It has been demonstrated that a direct relationship exists between the increase in the number of pollutant particles in the air and the thickness of inner artery walls (the "intima media"), which is a proven indicator of arteriosclerosis.

Stringent clean air regulations would contribute to a widespread improvement of health standards.

Another concept which is often the subject of debate is ozone and the ozone layer, but what exactly is it? All of us know that ozone protects us from ultra-violet radiation from the sun, but we do not always understand what it actually consist of. Ozone is a molecule of oxygen made up of three atoms of oxygen instead of the two atoms forming common oxygen, but more importantly, it can be said that without this gas, our lives and that of the organisms that surround us would be condemned to disappear.

Therefore, ozone is of vital importance for our survival and must necessarily be safeguarded – such is the purpose of our study.

2. AIM OF THE STUDY

Highly aware of the problems of environmental pollution and with the hope that our work would serve as an example, we set out to create ceramic decoration vehicles with a drastic reduction in COD levels. Our aim represented a significant challenge, as not only did it comprise developing a new range of vehicles for screen printing, rotogravure and flexography, but it also called for cost constraints in line with the current situation of the market.

3. DEVELOPMENT

The work guidelines we established demanded that the first target should be completed before proceeding to the second stage. This first target is outlined below.

3.1. First target.

Given the complexity of obtaining COD readings, the IPROMA analytical laboratory, accredited by Spain's National Accreditation Body (ENAC) according to EN standard 17025, was selected as the reference laboratory.

This analysis was carried out in accordance with the EA/011-m method.

A series of vehicles for screen printing and another series for rotogravure were taken and analysed to determine the COD (Chemical Oxygen Demand) value of the raw materials. This analysis of thirty different raw materials indicated that the highest COD value corresponded to glycols – indeed, the formulae used contained four different glycols (i.e. derivatives of ethylene oxide).

Glycols ($HO-CH_2CH_2-OH$) are systematically known as ethan-1,2-diol. This is in fact the simplest diol, a name which is also used for any polyol. The name comes from the Greek *glykos* (sweet) and refers to the sweet taste this substance has. As a result of its sweet taste, it has been used fraudulently to increase the sweetness of wine while also evading tests to identify added sugars. However, it is toxic for humans and can cause kidney failure.

Glycol is a colourless, odourless and slightly viscous substance with a high boiling point and a melting point of approximately -12 ºC (261 K). It mixes with water in any proportion.

These products are given a generic name in the flexible polyurethane sector of 'Polyol'.

It is also used as an anti-freeze additive for internal combustion engine cooling systems; it is a main constituent of vehicle brake fluid and is also used in chemistry in the synthesis of polyurethane or certain polyesters, as a base product when synthesising dioxane, glycol monomethyl ether or glyco dimethyl ether, as a solvent, etc.

Glycol is obtained industrially by oxidising ethylene in the presence of silver oxide as a catalyst, followed by hydrolysis of the ethylene oxide generated in the first stage. Another way of synthesising glycol is by stereochemistry using a cold, diluted base solution of potassium permanganate (permanganate hydroxylation).

In the ceramic sector - the subject of our concern – the glycols most frequently used in vehicles are as follows:

- Screen printing ⟶ DEG (diethylene glycol) or PEG400 (polyethylene glycol-400).
- Rotogravure ⟶ MEG (monoethylene glycol).

Which leads to the conclusion that the greater the percentage of glycol present in the final formula, the higher COD reading the end product will give.

Therefore, once all the glycols had been characterised, a search, based on our own experience, began for less pollutant alternatives.

Table 1 shows the comparison of the most common glycols and a summary of the most significant alternatives.

RAW MATERIAL	COD (mg O_2/l)
GLYCOL 1	576.000
GLYCOL 2	840.000
GLYCOL 3	629.000
GLYCOL 4	596.000
ALTERNATIVE 1	No medible
ALTERNATIVE 2	100.000
ALTERNATIVE 3	8.000
ALTERNATIVE 4	53.000

Table 1. COD analysis.

The results illustrate clearly the significant difference that exists between standard glycols and their alternatives. Of all the alternatives tested, three were found to be valid for the purposes of this study, which enabled us to consider the first objective as achieved and proceed to the next one.

3.2. Second target.

This consisted of using the results of the first stage to formulate vehicles for screen printing and rotogravure.

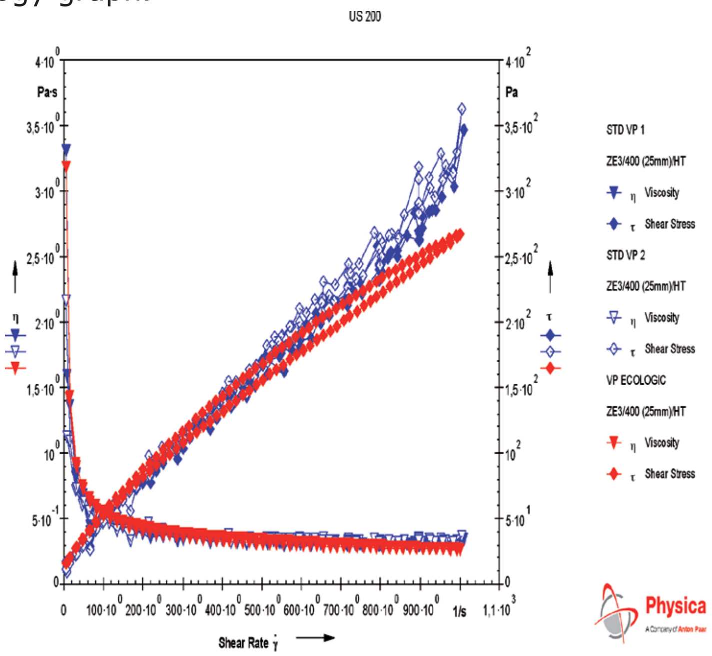
The first task was to gradually substitute the glycols with the various alternatives, without forgetting that the end product had to maintain the same properties provided by the glycols (good rheology, improved suspended solids, low vapour pressure, moistening of the substrate and the ceramic powder, anti-foaming agent,...). In the end, Alternative 4 was found to resemble a ceramic decoration vehicle most closely with guaranteed reproducibility and long-term stability.

The following is the detailed development of the vehicle for screen printing and rotogravure:

3.2.1. Screen printing vehicles (traditional and self-fixing).

An objective of obtaining vehicles which would give a pseudoplastic rheology when impasted with screen printing and pigment in a solids/vehicle ratio of 100:70-90 respectively was established in order to provide for proper definition, to prevent on-screen evaporation to avoid clogging and hue changes, and to ensure correct absorption onto the ceramic piece depending on the type of product to be made.

A Physica MC1 rheometer with a ZE4 spindle at 25ºC temperature was used to plot the rheology graph.



Graph 1. Rheology comparison.

Graph 1 clearly depicts how both standard vehicles taken as reference models and the new proposed vehicle all have the same rheology, i.e. a pseudoplastic rheological behaviour that allows for good definition.

The following equipment was used to measure the parameters given in the next table:

- A 100 ml certified and calibrated pycnometer.
- A Selecta Brookfield ST-2001 viscometer: Spin 2, 30 rpm.
- A certified and calibrated Ford cup with a 6 mm opening.
- A Crison Basic 20 pH-meter.

		% GLYCOL SUBSTITUTION					
	PARAMETERS	0	10	30	50	70	100
PRODUCT	Density (g/l)	1.097	1.100	1.119	1.128	1.137	1.145
	η (cPs)	350	345	329	322	315	308
	η CP6 (˝)	53	53	52	50	49	47
	pH	8.1	8.2	8.4	8.5	8.7	8.9
SCREEN PRINTING INK	Density (g/l)	1.605	1.613	1.621	1.628	1.635	1.647
	η CP6 (˝)	26	28	30	39	44	50

Table 2. Physical parameters.

Table 2 shows that as the new combination of raw materials substitutes glycol, product density and pH increase while viscosity diminishes, although viscosity in the ink increases. This does not represent any difficulty as it can be corrected fairly easily by reducing the percentage of thickeners.

3.2.2. Rotogravure vehicles.

The objective set here was more tedious as over 200 different compositions were made and when a stable vehicle had finally been obtained, it then proved to be troublesome with regard to ink sedimentation; when a perfect ink suspension was obtained, the vehicle was unstable or the inks would not discharge, etc. Eventually, all the compositions were screened to obtain a vehicle that would be stable over time with optimum ink discharge, maximum suspended solids and suitable drying.

The values in the following table were obtained at 25ºC and show the physical parameters for two standard vehicles on the market and the trial alternative. The following equipment was used for these measurements:

- A 100 ml certified and calibrated pycnometer
- A Selecta Brookfield ST-2001 viscometer: Spin 1, 100 rpm
- A certified and calibrated Ford cup with a 4 mm opening
- An iFi DST-100 Surface Tension Analyzer
- A mercury thermometer.

	VH 1 STD	VH 2 STD	ECOLOGIC VH
Density (g/l)	1,090	1,070	1,115
η Brookfield cPs	72	105	83
η CP4 (˝)	13	16	14
α (dynas/cm)	36.3	39.5	38.5

Table 3. Physical parameters

In the above table, it can be seen that the new formulation returns intermediate values between the two standard vehicles in both viscosity and surface tension and can easily be adapted to meet the customer's technical requirements.

The following equipment was used to determine separation and ink sedimentation:

- Glass test tubes.
- Mercury thermometer.

Initially, the test-tubes were filled up to 10 cm with ink at 25ºC.

The following table shows the physical values for the inks prepared with a solids/vehicle ratio of 100/100 respectively, in which the solids were prepared as follows (25/75 screen printing base/pigment) and measured at 25ºC.

	STD 1 VH	STD 2 VH	ECOLOGIC VH
Density (g/l)	1,705	1,698	1,718
η Brookfield cPs	280	335	305
η CP4 (˝)	19	23	20

Table 4. Ink characterisation.

		VH STD 1	VH STD 2	VH ECOLOGIC
1 day	Separation	0 cm.	0 cm.	0 cm.
	Sedimentation	Non-existent	Non-existent	Non-existent
1 week	Separation	1 cm.	1.5 cm.	0 cm.
	Sedimentation	Non-existent	Non-existent	Non-existent
2 weeks	Separation	2 cm.	2 cm.	0.5 cm.
	Sedimentation	Ligero endurec.	Slight hardening	Non-existent
1 month	Separation	3 cm.	3 cm.	1 cm.
	Sedimentation	Hardening	Slight hardening	Non-existent
2 months	Separation	4.5 cm.	3.5 cm.	1 cm.
	Sedimentation	Hard	Hardening	Non-existent
6 months	Separation	5 cm.	4 cm.	1 cm.
	Sedimentation	Hard	Hardening	Non-existent

Table 5. Evolution of ink separation-sedimentation.

In table 4, it can be seen that, in the newly developed product, ink viscosity is closer to the lowest value obtained with a standard vehicle and therefore gravity-produced separation and sedimentation would be more likely, whereas table 5 shows how sedimentation and separation evolve when measured in cm, where the new product provides more stable separation and sedimentation over time.

Now that the second objective had been achieved, a third target was left to tackle which, although somewhat insignificant in terms of percentage of component in the formula, is nevertheless important as far as the results are concerned. This third objective consisted of eliminating the bubbles and micro-foam created in this new formulation. This problem took over two months of countless trials to correct until a successful way of eliminating bubbles and micro-foam could be found.

With the third target successfully concluded, we proceeded to carry out trials on both domestic and international customers' products and after several months of small adjustments, the desired outcome was finally achieved.

Given that the main objective of this work was to achieve a drastic reduction of organic pollutants in waste waters, which then affect natural water resources, the time has come in the authors' opinion to publish this research.

Table 6 below shows the COD values for vehicles with STD formulations representative of the present market compared with our research product, named **ECOLOGIC**:

	STD 1 VH	STD 2 VH	STD 3 VH	STD 4 VH	ECOLOGIC VH
COD (mg O_2/l)	668,000	629,000	844,000	576,000	<250,000

Table 6. COD readings in different vehicles.

The table shows that our new development reduces COD by half in the least favourable case and even provides reduction rates of up to 70 %.

N.B.: We have successful developments with COD values of less than 80.000 mg O_2/l, but they are very close to the limit with regards to stability and a wide working range.

4. CONCLUSIONS

Having analysed Graph 1 and the various tables, the following conclusions can be drawn:

1. Similar rheology was reproduced in a screen printing vehicle while all other parameters remained the same.
2. We were able to produce a rotogravure vehicle with identical viscosity (in both the product and the ink) and surface tension.
3. We significantly improved suspended solids over time in a rotogravure vehicle.
4. We minimised colour transfer between rollers due to increased ink adherence in the rotogravure application.
5. We increased the effective working range with this new formulation concept.

6. The main objective of our research was comfortably achieved – COD was seen to drop drastically in our **ECOLOGIC** product compared with that of other vehicles on the market. This represents a quantitative breakthrough in terms of environmental improvement and cost savings in the management of wastewater pollutants.
7. The line of research employed herein that has led to such successful results is merely the tip of the iceberg: we are therefore even more motivated to continue working on improving and preserving the environment.

REFERENCES

[1] ATC. Tecnología de fabricación de azulejos. 1990.

[2] SACMI IMOLA. Tecnología cerámica aplicada. 2004.

[3] MORALES GÜETO, Juan. Tecnología de los materiales cerámicos. 2005.

[4] MONFORT, E.; CELADES, I.; MALLOL, G. Cuestiones básicas sobre medioambiente para un técnico del sector cerámico. Instituto de Tecnología Cerámica-AICE. Castellón, 1999.

[5] ASH, Michael and Irene. Lubricants. Synapse Information Resources, Inc. 2001.

[6] BLASCO ALBERTO, Javier. Curso de reología aplicada. Universidad de Zaragoza. 2006.

[7] LANSDOW, A. R. Lubrication and Lubricant selection. 2004.

[8] GUNDERSON, R. C. and HART, A. W. Synthetic Lubricants, Reinbold. New York, USA. 1962.

[8] MORTIER, R. M. and ORSULLIK, S. T. Chemistry and technology of lubricants. 1992.

[10] UNIVERSIDAD DE NAVARRA. Análisis de aguas potables y residuales. 2007.

[11] HOUGEN, Watson and Ragatz. Principios de los procesos químicos. Editorial Reverté, S.A. España 1972. Tomo I. Balances de Materia y Energía.