Jungbunzlauer

From nature to ingredients®

facts

CITROFOL® as coalescent agent

Introduction

The paint and coatings industry, which is primarily divided on the basis of composition, application and functionality, and further subdivided into different segments such as packaging, automotive, marine, electronics and architectural, plays an important role in all areas of life. Virtually all of us are exposed to paints and coatings, which is why toxicologically and environmentally safe solutions are paramount for manufacturers and consumers.

As one of the world's leading producers of biodegradable ingredients using renewable resources, Jungbunzlauer enables its customers to manufacture healthier, safer and more sustainable products. The company is one of the largest global producers of citric acid and citrate esters, which it markets under the well-known brand name CITROFOL®. Citrate esters have an excellent toxicological and eco-toxicological profile, but also provide good versatility and compatibility with numerous polymers including paint and coating components. They are particularly characterised by highly efficient solvation, low migration and non-VOC (volatile organic compound) attributes. CITROFOL® grades offer a sustainable alternative to petrochemical-based coalescent agents and similar solutions.

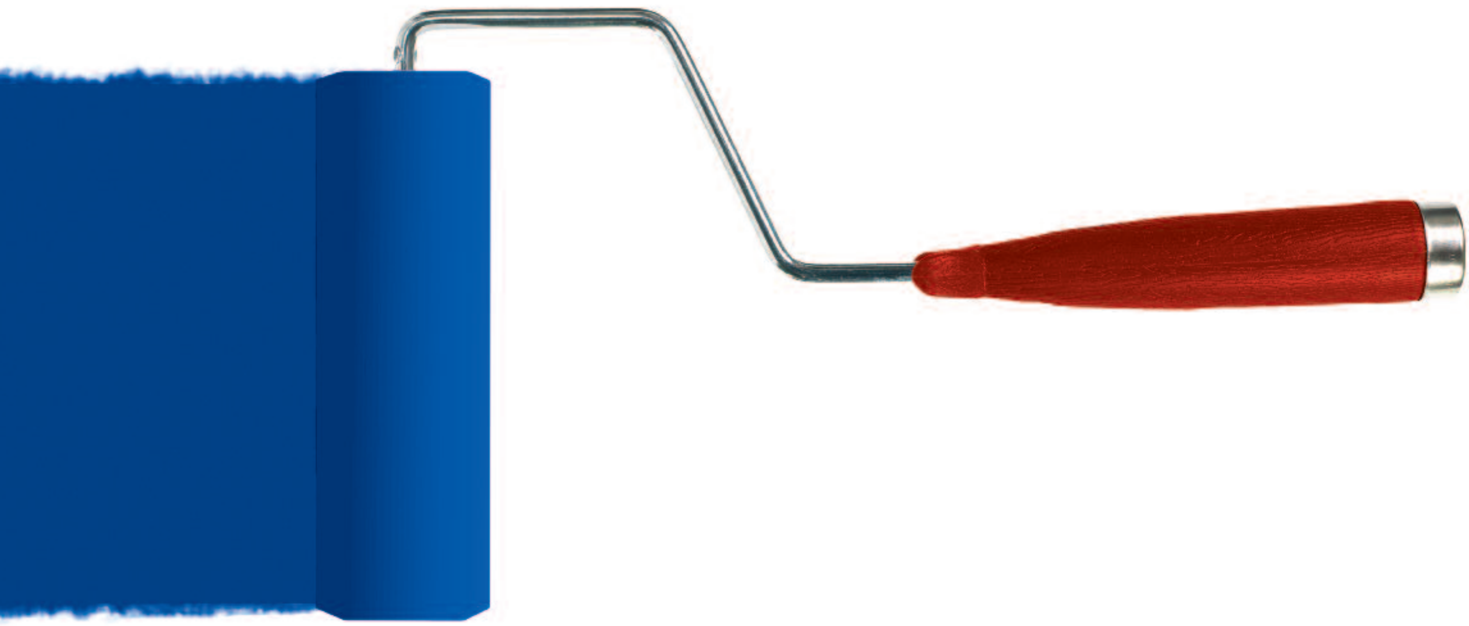
Function of coalescent agents

In a very simplified form, liquid coatings consist of a dispersion medium which carries the polymer particles that will eventually form the coating layer. The dispersion medium may be an organic solvent, although today's preferred option is water. After the application of a coating onto a surface the dispersion medium evaporates, causing the polymer particles to draw together. When the polymer particles come into contact, the coalescent agent takes effect, giving rise to the formation of a homogeneous film. In practice this interaction is more complex and is influenced by various factors, in particular the nature of the polymer, which might be an acrylic, poly urethane or other.

Coalescent agent mandatory requirements and trends

The main function of a coalescent agent is to guarantee uniform and optimal film formation for the desired mechanical performance (e.g. scrub resistance and film hardness) and aesthetic values (e.g. gloss and haze effects). In the past the preferred coalescent agents generated a film with a high degree of hardness after evaporation but were highly volatile. Today, high volatility is considered an undesired effect, with volatile organic compounds (VOCs) contributing to emissions and causing hazardous conditions for paint manufacturers and processors, not to mention interior architectural paints and the adverse effects they can have on consumers.

In addition to meeting the current demand for non-VOC products, CITROFOL® esters from Jungbunzlauer fully satisfy the latest toxicological and environmental safety requirements.



VOC versus non-VOC
Each liquid exhibits a characteristic volatility, which is determined by its vapour pressure. A high vapour pressure corresponds to a low boiling point, and a low boiling point causes a vast amount of molecules to evaporate even under ambient conditions. Depending on the particular substance, VOCs can be harmful to human health or the environment. There is, however, no standardised global definition of what constitutes a VOC. The European Union defines a VOC as “any organic compound having an initial boiling point less than or equal to 250°C (482°F) measured at a standard atmospheric pressure of 101.3kPa”.

The applicability of paint formulations with coalescent agents that are classed as VOCs is very restricted, especially for indoor use. With indoor regulations becoming ever stricter, there is a clear trend towards “low VOC” or even “zero VOC” formulations.

Table 1 shows the origin, boiling points, odour and required safety labelling according to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) for citrate esters and standard coalescent agents.

Table 1: Comparison of properties of classical coalescent agents vs. citrate esters

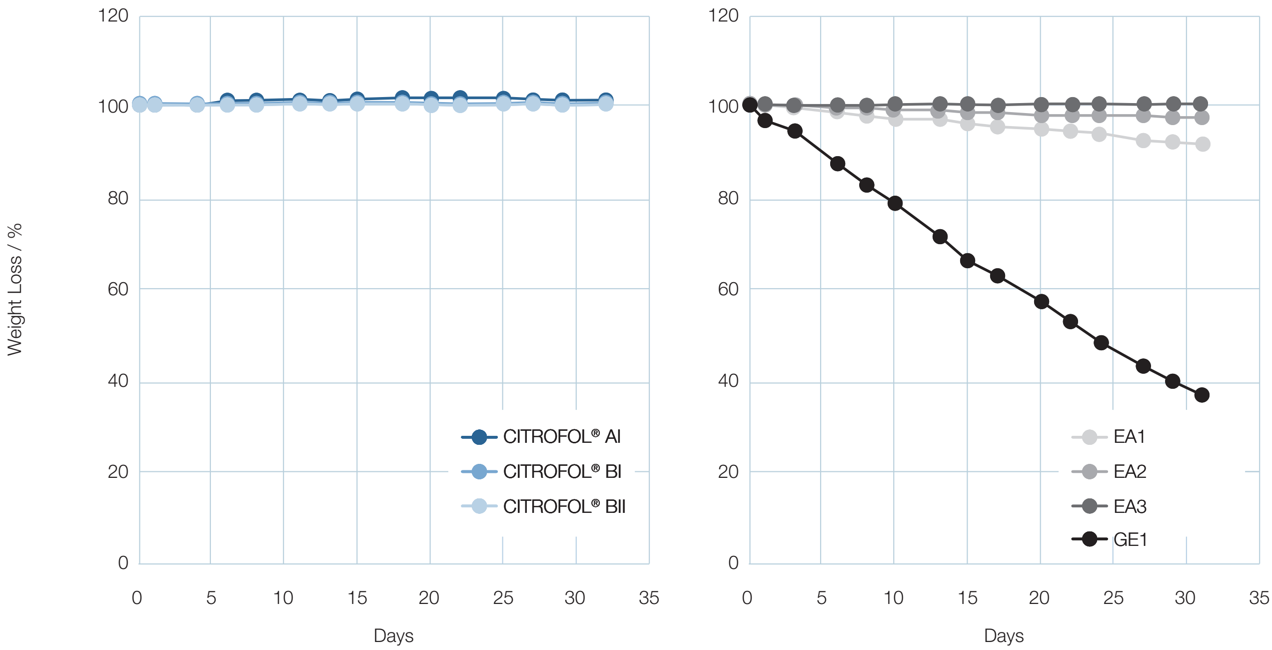
	Esteralcohol			Glycolether	Citrate ester
Chemical Composition	2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate **(EA1)**	2,2,4-Trimethyl-1,3-pentanediol diisobutyrate **(EA2)**	2,2'-Ethylendioxy-diethyl-bis (2-ethylhexanoat) **(EA3)**	Dipropylenglycol-n-butylether **(GE1)**	Tributyl O-acetylcitrate **(CITROFOL® BII)**
Origin	fossil	fossil	fossil	fossil	bio-based
Boiling Point (@ 101.3kPa)	262°C	282°C	351°C	230°C	331°C
VOC	yes / no*	yes / no*	no	yes	no
GHS			no	no	no
Odour	weak odour	odour	odourless	odour	odourless

*Depending on the regulation

All citrate ester grades are considered non-VOC. The fact that CITROFOL® esters are bio-based, odourless and label-free represents a great advantage over conventional coalescent agents.

Figure 1 illustrates the volatility of CITROFOL® citrate esters and conventional coalescent agents. Weight loss was determined over a period of 28 days under ambient conditions.

Figure 1: Volatility of different CITROFOL® types (left) and conventional coalescent agents (right)



No citrate esters showed weight loss over a period of 28 days, whereas the conventional coalescent agents EA1, EA2 and GE1 evaporated over time. The volatility of the CITROFOL® grades is therefore significantly lower, as already indicated by their higher boiling point. This is a very important requirement for low VOC applications.

CITROFOL® in clear coatings

Background
The performance of the citrate esters in real formulations was investigated. Aqueous clear-coat formulations were chosen as the first test systems, since their lower number of components allows better assessment of the influence of CITROFOL®. We tested different types of dispersions in formulations suitable for applications in the area of wood coatings and metal coatings.

From a technological perspective the main goal was to produce homogeneous, tack-free coatings in order to be able to apply the relevant characterisation methods. The appropriate optimum or optimum range of filmforming agents was then selected and the resulting films were characterised.

Preparation and application procedure for clear coat formulations
The coalescent and defoaming agents were added to a dissolver containing 40g of dispersion while stirring. The mixture was then stirred for about 5 minutes at 2500rpm with a toothed disc. Subsequently, the mixture was allowed to rest for at least 24 hours before the dispersion was applied, to ensure that the formulation was free of air bubbles.

A doctor blade (120µm) was used to apply the coatings. The coating was applied to glass or steel substrates and then dried for at least 96 hours at room temperature. A final dry film thickness of approximately 60µm was achieved.

Test methods
All formulations were analysed for pendulum hardness, gloss and adhesion properties.

Pendulum Hardness
Pendulum hardness was measured according to König (DIN EN ISO 1522). In this test method, a pendulum with two stainless steel spheres is placed on the dried coating. Once the pendulum is oscillating, the spheres move over the coating surface, exerting pressure on the coating. The softer the surface, the more the pendulum is damped and the fewer the pendulum oscillations recorded. In the case of the clear coatings the applied coating formulations were dried for at least 96 hours at room temperature.

Optical Properties – Gloss
The gloss measurements were taken using a glossmeter in accordance with DIN EN ISO 2813:2015-02. Depending on the surface properties and on the anticipated gloss range, gloss will be measured at 20° (high gloss surface), 60° (medium gloss) or 85° (low gloss surface).

Cross-Cut Test
The cross-cut test is a simple and economic method for evaluating the adhesion of single- or multi-coat systems. The cross-cut tests were carried out in accordance with DIN EN ISO 2409. With this method, six parallel cuts are carved into the coating with a cross-cut knife. Another six cuts are then made at 90° angles to the previous cuts. Adhesive tape is applied firmly to the resulting square pattern and then pulled off briskly. The remaining grid is inspected visually and can be graded using a standard table. Adhesion is evaluated on a 0 to 5 scale. Good coatings show high adhesion with values between 0 and 1 whereas poor coatings result in low adhesion with values between 3 and 4.

Results

Table 2 summarises the final test results for the dispersions Acronal® Pro 760 (BASF) and ALBERDINGK® AC 2403 (Alberdingk Boley). It was not possible to incorporate the benchmark product EA3 into the Acronal® Pro 760 dispersion, so no application tests are available for this combination. The incorporation of EA1, CITROFOL® AI and CITROFOL® BII at a concentration of 2% resulted in homogenous, closed films.

Generally, the properties of the coatings based on CITROFOL® are comparable to coatings based on EA1. However, CITROFOL® AI showed improved pendulum hardness and CITROFOL® BII slightly improved gloss properties as compared to EA1.

In the case of the ALBERDINGK® AC 2403 dispersion it was possible to incorporate EA1, EA3, CITROFOL® AI, CITROFOL® BI and CITROFOL® BII. All tested citrate esters showed adhesion and gloss results similar to the EA1 and EA3 formulations. CITROFOL® AI resulted in improved pendulum hardness. Slightly lower but still acceptable hardness values were obtained with CITROFOL® BII.

In addition to the dispersions for metal coatings we investigated a variety of dispersions suitable for wood coatings, e.g. Joncryl® 8331, ALBERDINGK® AC 3630 and ALBERDINGK® AC 3660. The results are available on request. Due to the differing chemical and colloidal nature of dispersions it is not possible to predict general compatibility with particular coalescent agents. However, based on the results we obtained in this study we can confirm that our CITROFOL® grades are highly compatible with acrylic dispersions.

Table 2: Results of application tests for Acronal® Pro 760 (above) and ALBERDINGK® AC 2403 (below)

Acronal® Pro 760 (BASF)				
Coating properties	**EA1 2%**	**EA3**	**CITROFOL® AI 2%**	**CITROFOL® BI 2%**
Compatibility	✔	✖	✔	✔
Hardness	Reference I	Reference II	↑	→
Adhesion			→	→
Gloss			→	↗

ALBERDINGK® AC 2403 (Alberdingk Boley)					
Coating properties	**EA1 5%**	**EA3 5%**	**CITROFOL® AI 3%**	**CITROFOL® BI 5%**	**CITROFOL® BII 5%**
Compatibility	✔	✔	✔	✔	✔
Hardness	Reference I	↓	↑	↘	→
Adhesion		→	→	→	→
Gloss		→	→	→	→

■ Better than benchmark EA1 ■ Equal to benchmark EA1 ■ Worse than benchmark EA1

CITROFOL® in architectural paints

Background

After the very encouraging results from the clear-coat project, it was decided to undertake an extended investigation of CITROFOL® as a coalescent agent in a more complex formulation. The architectural paint formulation chosen for this purpose represents an important global market segment. Special requirements specific to the use of VOCs in architectural paints justify the use of CITROFOL® as a coalescent agent.

Paint preparation process and formulation recipe

A standard, flat architectural paint formulation acted as the basis for the test formulation. A detailed description of the formulation can be found below in table 3. The preparation process consisted of three main steps:

In the first step, the rheology modifier was dissolved in water before the dispersing agent, the wetting agent, the defoamer and the neutralisation agent for the resin were added while stirring moderately.

The second step was the grind stage. Here, pigments, fillers and other additives were added and ground under high shear using ZrO2 (zirconium dioxide) milling beads until the appropriate grind rating was achieved.

The third step comprised the letdown or thindown phase, in which the grind is diluted with the remaining, less viscous formulation components like the binder and the coalescent agent. The letdown components were added sequentially by stirring them into a vessel containing the grind mix. The milling beads were then removed from the mixture by sieving.

Throughout this study the concentration of the coalescent agent was kept constant at 2.4% (based on the total formulation). Different CITROFOL® grades (CITROFOL® AI, BI, BII) were tested and the properties were compared to conventional coalescent agents like EA1, EA2 and GE1.

Jungbunzlauer's citrate esters differ in their molecular structure and molecular weight which results in different polarities and volatilities. This makes them ideal candidates to fulfil the different requirements of paint formulations.

Table 3: **Flat paint formulation used for the evaluation of the effect of the citrate esters/coalescent agents on the paint properties**

Component	Supplier	Function	Parts by weight/g
1st step: Mixing low shear 10 minutes, 500rpm			
Water (deionised)		Solvent	21.3
Natrosol™ 330 Plus	Ashland	Rheology modifier	0.5
AMP-95™	ANGUS Chemical Company	Amine for resin neutralisation	0.2
Orotan™ 1124	DOW	Dispersing agent	0.5
Tego® Foamex 8030	Evonik	Defoamer	0.2
Carbowet GA-100	Evonik	Wetting agent	0.2
2nd step: Grind stage pigment preparation high shear 30 minutes, 4000rpm			
TiPure R-706	Chemours	TiO_2 white pigment	18.8
ImerCarb™ 10	Imerys	$CaCO_3$ filler	9.4
Minex® S-4	Sibelco	Functional filler	9.4
Diafil® 525	Imerys	Matting agent	4.2
3rd step: Letdown—low shear—10 minutes, 1000rpm			
Acronal® S 790	BASF	Binder	31.5
Tego® Foamex 1488	Evonik	Defoamer	0.2
Acrysol RM-2020E	DOW	Rheology modifier	1.5
CITROFOL® BII	**Jungbunzlauer**	Coalescent agent	2.4
			100

Characterisation methods

All formulations were analysed for drying behaviour, pendulum hardness, gloss, and wet-scrub resistance. In addition, viscosity measurements and various application methods like sagging and levelling were carried out to evaluate the influence of citrate esters versus conventional coalescent agents on the paint properties.

The test procedures for the determination of pendulum hardness and gloss are described in detail in the former paragraph test methods. For pendulum hardness, the architectural paint formulation samples were dried for one day at room temperature.

Wet-Scrub Resistance

The wet-scrub resistance was measured according to DIN EN ISO 11998:2006-10. This quantifies the resistance of the coating to repeated wet-abrasive cleaning procedures.

In this test the paint to be evaluated is applied to a black plastic scrub panel at the respective wet film thickness and allowed to dry for 28 days at 23°C ± 2°C and 50% ± 5% relative humidity. The sample is then scrubbed using an appropriate pad and washing-up liquid. The test is ready for evaluation after 200 wet-scrub cycles in a scrub testing machine.

The classification of wet-scrub resistance is done via the mass loss of the sample. Because the scrubbed area is known, the reduction in thickness can be calculated and classified according to a rating scale (DIN EN 13300). The classification is summarised in table 4.

Table 4: Classification according to DIN EN 13300

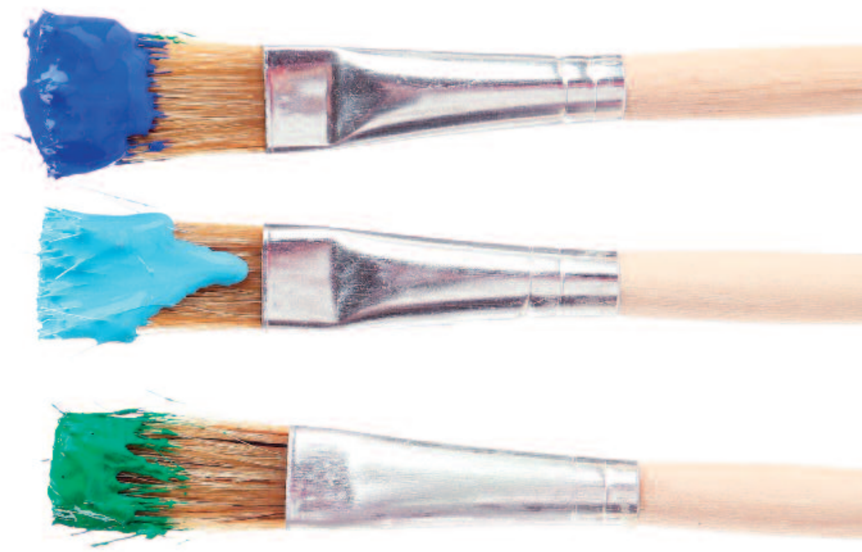
Class	Wet-scrub thickness reduction	Scrubs
1	< 5µm	200
2	≥ 5µm to 20µm	200
3	≥ 20µm to 70µm	200
4	< 70µm	40
5	≥ 70µm	40

Drying behaviour
The drying behaviour of a sample can be quantified based on different degrees of drying. This is measured in accordance with DIN EN ISO 9117-5:2012 and distinguishes between seven drying stages (DS 1–7). For this study, the drying degrees 1, 4 and 7 were evaluated. This involved three different measurement procedures described in the relevant norm.

Viscosity
A rotational rheometer (Haake™ RheoStress™ 1, Thermo Fisher Scientific) was used to measure the viscosity of the paint formulations. The shear rate varied between $0.1s^{-1}$ and $1000s^{-1}$. During measurement the temperature of the sample was kept constant at 25°C.

Levelling & Sagging Test procedure
Levelling is evaluated using a Leneta draw-down blade, which is a special doctor blade with five pairs of notches with different gap sizes (0.1, 0.2, 0.3, 0.5 and 1.0mm). For the levelling, the substrate is kept in a horizontal position after the paint application. It is rated according to the separation of merges of the corresponding pairs of stripes. The rating scale ranges from 0 (poor) to 10 (excellent).

Sagging is also evaluated using a Leneta draw-down blade, which forms 10 streaks of paint of varying thickness values (75-300µm) on the substrate. After paint application the substrate is held in a vertical position. Sagging is defined by the thickest paint stripe that does not show sag.



Test results

All test results are summarised in table 5.

Table 5: Summary of all application tests performed with the architectural paint formulation

Film forming agent	Pendulum hardness in seconds	Gloss 85° (GU)	Thickness reduction in µm after 200 scrub cycles	Wet-scrub resistance class	Levelling	Sagging	Viscosity in Pas ($0.1s^{-1}$)
EA1	10	2.3	3.18 ± 0.12	1	0	10	287
EA2	11	2.1	3.11 ± 0.30	1	0	10	297
GE1	9	2.3	3.61 ± 0.10	1	0	10	206
CITROFOL® AI	9	2.4	3.62 ± 0.15	1	0	10	333
CITROFOL® BI	8	2.4	3.62 ± 0.20	1	0	10	242
CITROFOL® BII	13	2.3	3.64 ± 0.17	1	0	10	248

The deviations between the tested coalescent agents for the dried paint formulations were not significant. The values obtained for pendulum hardness and gloss were very low. This corresponds to the typical appearance of an interior flat paint formulation.

In the case of wet-scrub resistance, the thickness loss after 200 scrubbing cycles varied between 3.1µm and 3.6µm for all samples, which is quite low. Therefore all tested formulations fall into abrasion class 1 according to DIN EN 13300. These values show that no citrate esters have a negative impact on the wet-scrub resistance of the paint formulations.

As regards drying behaviour, the formulations with EA1, CITROFOL® AI and CITROFOL® BII yielded identical results which are quantified in degrees of drying as mentioned above. The degree of drying DS1 (dust-dry) was reached after 15 minutes. DS4 was achieved after 30 minutes and DS7 after 60 minutes. Very similar results were obtained for levelling and sagging and for viscosity measurements, too.

Summary

The CITROFOL® citrate esters have great potential as coalescent agent alternatives in water-based coatings and paint systems. This study revealed that CITROFOL® exhibits the same or even better results compared to the standard coalescent agent EA1 as regards all crucial processing requirements and end-product properties. The citrate esters showed broad compatibility with different types of dispersions designed for a variety of applications including metal, wood, and architectural coatings.

CITROFOL® citrate esters proved to be successful in both clear and pigmented coatings. All tests indicated their performance equalled or was even better than that of the glycol ether and ester alcohol benchmarks. Apart from having the typical coalescent agent attributes, all CITROFOL® types are non-VOCs, odourless, colourless, bio-based, toxicologically safe (free of hazardous labels) and environmentally friendly.

About Jungbunzlauer

Jungbunzlauer is one of the world's leading producers of biodegradable ingredients of natural origin. We enable our customers to manufacture healthier, safer, tastier and more sustainable products. Due to continuous investments, state-of-the-art manufacturing processes and comprehensive quality management, we are able to assure outstanding product quality.

Our mission "From nature to ingredients" commits us to the protection of people and their environment.

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