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## **The End of Guanidines? An Alternative Cure System for Neoprene 671A Liquid Dispersion**

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### **ABSTRACT**

Over the past several years, rumors have continued to swirl that guanidine accelerators, specifically 1,3-diphenylguanidine (DPG) and N,N'-di-ortho-tolylguanidine (DOTG), may no longer be allowed to be sold in Europe due to prospective REACH regulations. These products are commonly used in cure systems for polychloroprene latex. Since the future status of these accelerators is in doubt, it is important to develop new cure systems now. This paper investigates potential alternative cure systems for use in polychloroprene latex.

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## **Introduction**

On June 1, 2007, the European Union (EU) officially implemented the REACH directive, which consolidates older directives and provides for the Registration, Evaluation, Authorization, and Restriction of all Chemicals sold in the EU. Under this directive, chemical companies are required to register all chemicals imported, manufactured or sold in the EU for evaluation by the European Chemicals Agency (ECHA).

All manufacturers and importers of chemicals must identify and manage risks linked to the substances they manufacture and market....manufacturers and importers need to demonstrate that they have appropriately done so by means of a registration dossier, which shall be submitted to the Agency. Once the registration dossier has been received, the Agency may check that it is compliant with the Regulation....Where appropriate, authorities may also select substances for a broader substance evaluation to further investigate substances of concern.<sup>1</sup>

REACH includes within its scope existing chemicals which might be considered hazardous by today's standards. Rumors continue to circulate that under new REACH regulations, guanidines may no longer be allowed to be sold in Europe. Although these are currently just rumors, R.T. Vanderbilt Company has decided to start work on the development of alternatives to these accelerators. This paper investigates alternative cure systems for use in polychloroprene latex.

## **Neoprene**

Neoprene is the polymer of chloroprene (2-chlorobutadiene-1,3), or mixtures of majority chloroprene and other polymerizables. This polymer was first introduced to the rubber industry by Du Pont de Nemours & Company in 1931, where it became the first synthetic rubber to find wide commercial acceptance. A latex version of the product quickly followed. When properly compounded, polychloroprenes provide excellent resistance to degradation from heat aging, ozone, UV, abrasion, fire, and chemicals.

The crosslinking of Neoprene is fundamentally different than the crosslinking of natural rubber because the former requires the use of metal oxide (normally zinc oxide) instead of sulfur as the primary cure agent. The crosslinking takes place mainly at the sites on the polymer chain where there are "tertiary allylic chlorine atoms formed by the 1,2 polymerization of chloroprene monomer." The generally accepted theory is that the metal oxide initiates the curing process by forming metal chloride, which in turn reacts with neighboring polymer chains. Sulfur crosslinks may also occur at other sites on the chain.<sup>2</sup>

Accelerators play an important roll in the crosslinking of rubber. They affect both the rate of cure and the length and number of crosslinks that form. Accelerators are frequently classified based on the characteristics below:

Accelerator Type <sup>3</sup>	Cure Rate	Crosslink Length
None	Very Slow	Very Long
Guanidines	Moderate	Medium-Long
Mercaptobenzothiazoles	Moderate	Medium
Sulfenamides	Fast	Short-Medium
Thiurams	Very Fast	Short
Dithiocarbamates	Very Fast	Short

Table 1: Accelerator Comparison

As in other polymers, organic accelerators are used to enhance the physical properties of polychloroprene, although their effect is less pronounced. According to the literature, when high modulus is desired, the most effective accelerator in polychloroprene is diphenylthiourea (DPTU), either alone or in combination with diphenylguanidine (DPG). As shown in Table 1, guanidines such as DPG have a moderate rate of cure. Thioureas (DPTU) have a fast rate of cure, especially in halogenated polymers. Where high tensile strength is desired, the literature recommends equal parts of tetraethyl thiuram disulfide (TETD) and sodium di-n-butylthiocarbamate (NaDBC).<sup>4</sup> Thiurams and dithiocarbamates both have a fast rate of cure.

### Study

For this study a basic stabilization package was used along with 1.0 phr of Sulfur and 2.0 phr of Zinc Oxide.

### Masterbatch

Chemical	DRY	WET
<b>Neoprene LD617A</b>	100.0	170.0
Potassium hydroxide (10%)	0.5	5.0
<b>DARVAN® SMO</b> surfactant (33%)	0.5	1.5
<b>DARVAN WAQ</b> surfactant (33%)	0.25	0.75
Sulfur dispersion (50%)	1.0	2.0
<b>VANOX® L</b> dispersion (50%)	1.0	2.0
<b>Zinc Oxide Dispersion</b> (60%)	2.0	3.3
Polyacrylate thickening agent	---	2.0
Accelerator System (see table)	1.0-2.0	---

Table 2: Masterbatch

All quantities in the chart are in Dry (PHR).

	1	2	3	4	5	6 (control)	7	8	9	10	11
Diphenyl guanidine		1.0	2.0			1.0					
Diphenyl thiourea				1.0	2.0	1.0					
<b>ETHYL TUADS®</b> accelerator							1.0				
<b>BUTYL NAMATE®</b> accelerator							1.0				
<b>ISOBUTYL TUADS®</b> accelerator								1.0			
<b>SETSIT® 104EZ</b> accelerator									2.0		
<b>VANAX® PIC Slurry</b> accelerator										2.0	
<b>WB-12</b>											2.0

Table 3: Accelerator Systems

The films were coated on glass plates and allowed to dry for 24 hours. The films were then placed in the oven for vulcanization. The oven was allowed to rise to temperature for 4 minutes. The films were then cured for 30 minutes at 120°C. The films were then tested for unaged and aged (100°C for 22 hours) modulus, tensile, and ultimate elongation using an Instron® 3366 Universal Testing Machine. Additional uncured samples were tested for rheology using an Alpha Technologies MDR 2000.

## Results

Normally, one of the easiest ways to determine the state of cure of a latex article is to look at the tensile strength of the cured article. Since the overall goal is to replace the cure system in Compound 6, this will be used as the point of comparison.

	1	2	3	4	5	6	7	8	9	10	11
<b>Tensile (MPa)</b>	13.24	14.89	19.86	15.88	18.61	12.72	8.44	8.55	10.40	19.33	13.39
<b>Aged Tensile (MPa)</b>	19.98	26.21	24.12	19.49	22.93	23.11	22.93	12.51	18.15	25.58	29.89

Table 4: Tensile Results

Based on just the numbers, Compounds 1 (no accelerator), 2 (DPG), and 11 (WB-12) appear most similar to Compound 6. Of special note is Compound 10 (VANAX PIC Slurry), which provides excellent aged and unaged tensile results.

Another way to look at these results is graphically.

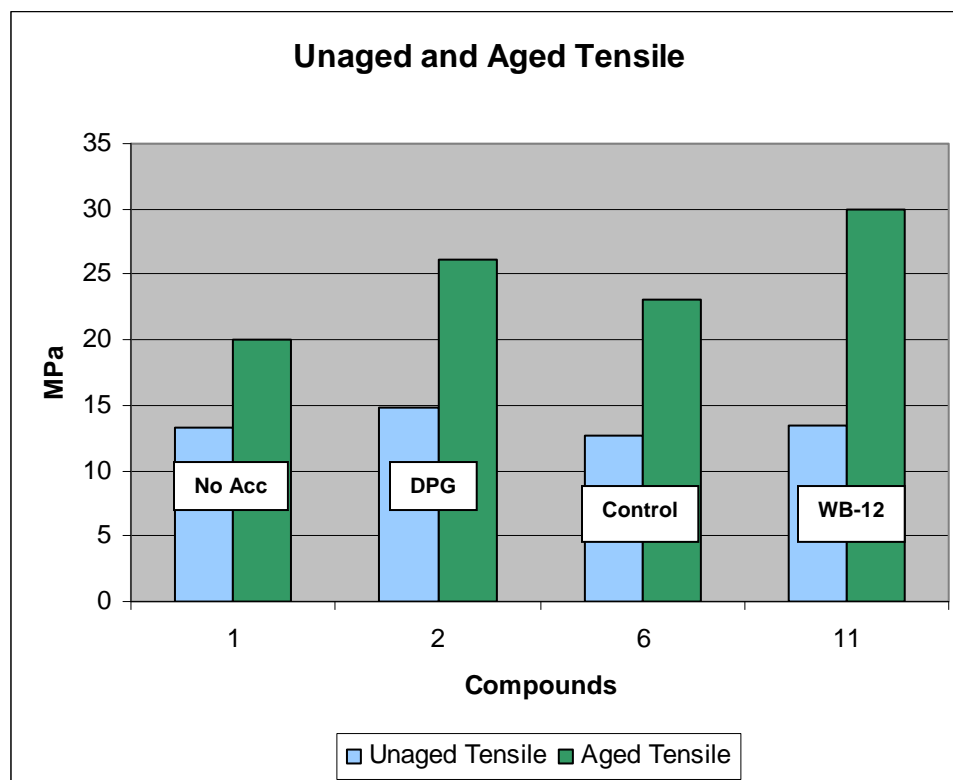


Figure 1: Aged and Unaged Tensile Strength

Since Compound 2 contains DPG, we can immediately rule it out as a possibility. This leaves Compounds 1 and 11. Since Compound 11 provides higher tensile both before and after aging, it seems that WB-12 is the best replacement cure system.

According to the literature<sup>5</sup>, and unlike in other latexes, tensile strength at break is not the most reliable measure of the state of cure of polychloroprene. This is mostly because, as the sample is cured, the

elongation decreases as the tensile strength goes through a maximum. Since the goal of this study is to determine which accelerators work best in polychloroprene, another more reliable measure of cure needed to be determined. Rheology, a test that determines the rate and state of cure, allows a more accurate determination of the optimal accelerator systems.

### Rheology

To understand rubber's dynamic properties, it is important to remember that it is neither perfectly viscous nor perfectly elastic. Instead it possesses both of these opposite response patterns simultaneously.

An example of a completely elastic material is an ideal steel spring. As a force is applied, the spring deforms in perfect synchronization with that force. This means that the deflection of the spring is at a maximum when the force is at its maximum. The spring also stores 100% of the energy expended during the spring's compression. The ratio of a spring's deformation to the force applied is a constant (characteristic spring rate). In rubber, both increased crosslink density and increased chain entanglements cause it to become more elastic.

Viscous materials also have a characteristic spring rate, which can be measured with a typical viscous damper, a cylinder filled with a fluid of moderate to high viscosity with a piston capable of movement within the cylinder. When a force is applied to the piston, it moves within the cylinder, causing the fluid to flow through the space between the piston and the wall of the container. This action also has its own characteristic spring rate; however, the flow of the viscous material translates all of the energy into heat, so none of the energy is stored. Additionally, unlike the ideal spring, the piston's motion is not synchronized with the application of the force. Its motion lags behind the maximum force. In rubber, this property relates to the pure flow of the rubber and it decreases with lower frequencies or higher temperatures.<sup>6</sup>

As mentioned above, at normal temperatures rubber is neither purely elastic nor purely viscous in its dynamic behavior. Deforming the material causes it to both store and dissipate some energy. This gives the material a complex dynamic spring rate. Figure 2 is commonly used to illustrate this complex relationship.

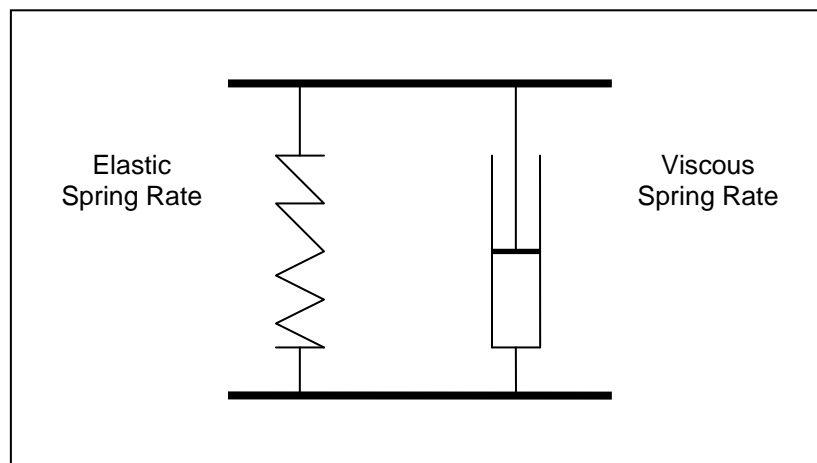


Figure 2: Mechanical model of the dynamic response in rubber

A Moving Die Rheometer (MDR) is one of the more common tools for the measurement of the visco-elastic properties of rubber. A rheometer is "a device which exposes a small sample of compound to vulcanization temperature and tracks its changes in viscosity as it cures to produce a kind of processing profile of the material."<sup>7</sup> For the purposes of this paper, we focused on  $M_H$ , the maximum torque/viscosity attained during a specific period of time. Samples were run at 120°C (248°F), 0.5° Arc, 60 min. clock according to ASTM D5289.

	1	2	3	4	5	6	7	8	9	10	11
$M_H$	5.09	5.34	5.71	5.80	6.53	5.78	5.80	5.68	5.83	7.65	5.87

Table 5: Maximum Torque,  $M_H$  Results

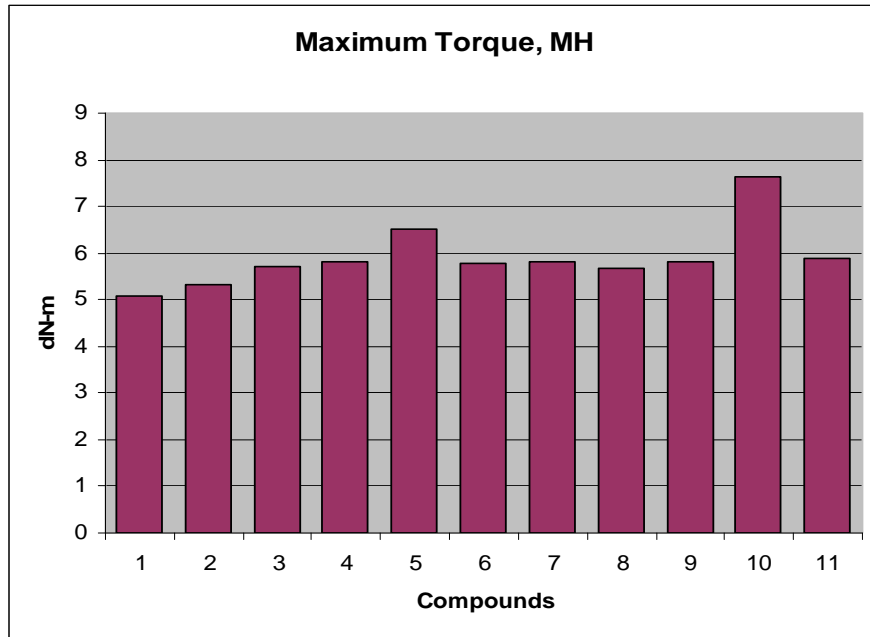


Figure 3: Maximum Torque,  $M_H$

Since the goal is to replace a specific cure system, it is simpler to look at the data relating to that cure system (Compound 6 (DPG/DPTU)).

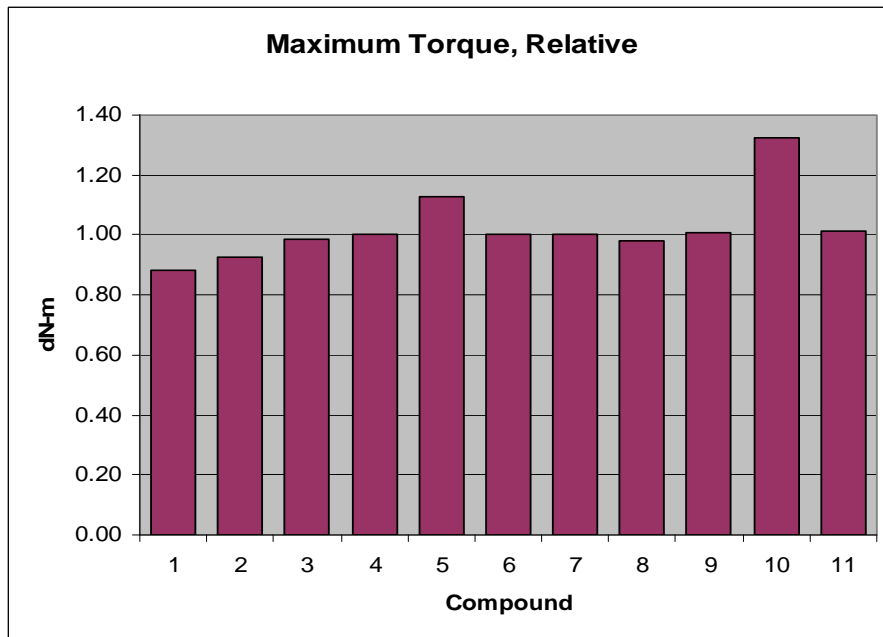


Figure 4: Relative Torque

Based on Figure 4, it is easy to see which cure systems provide equal  $M_H$  to Compound 6.

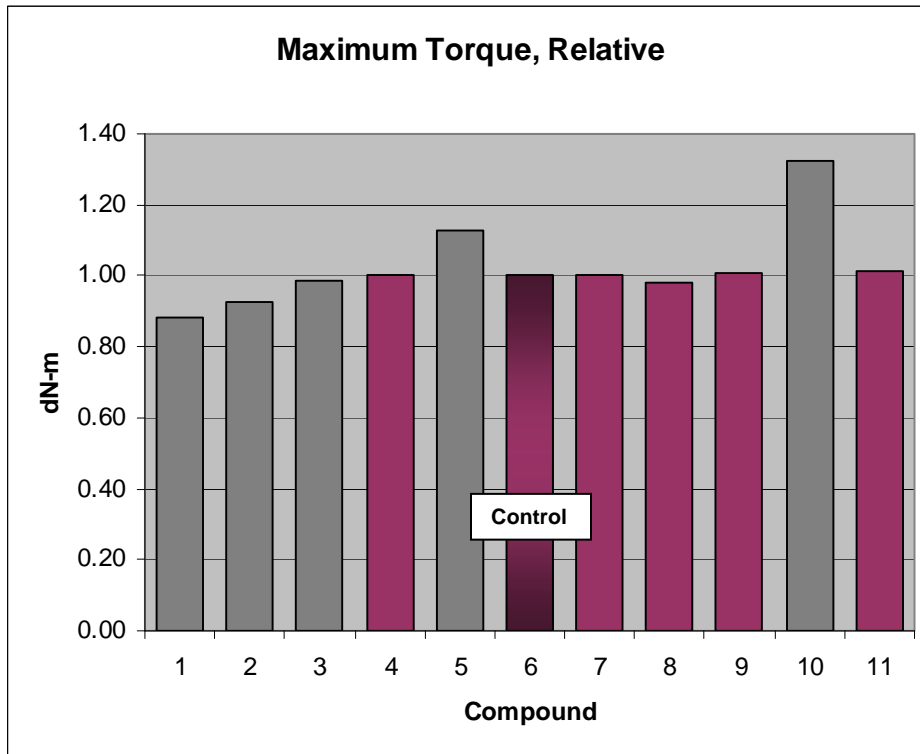


Figure 5: Relative Torque

Having ruled out Compound 3 (it contains DPG), it is easy to see that Compounds 4 (DPTU), 7 (ETHYL TUADS/BUTYL NAMATE), 8 (ISOBUTYL TUADS), 9 (SETSIT 104EZ), and 11 (WB-12) offer similar  $M_H$  values. Combining this information with the tensile results, WB-12, the accelerator package in Compound 11, is beginning to look like an excellent drop-in replacement. Of note is Compound 8, which contains ISOBUTYL TUADS. It shows a similar state of cure to the control but at only half the loading level (1.0 phr) of the control.

The final piece of the physical puzzle is modulus.

	1	2	3	4	5	6	7	8	9	10	11
Modulus (MPa)	1.29	1.43	1.64	1.47	1.71	1.59	1.16	1.25	1.06	1.61	1.35
Aged Modulus (MPa)	1.63	2.04	2.67	1.71	1.98	2.30	1.88	1.20	1.65	2.42	2.46

Table 6: Unaged and Aged Modulus Results

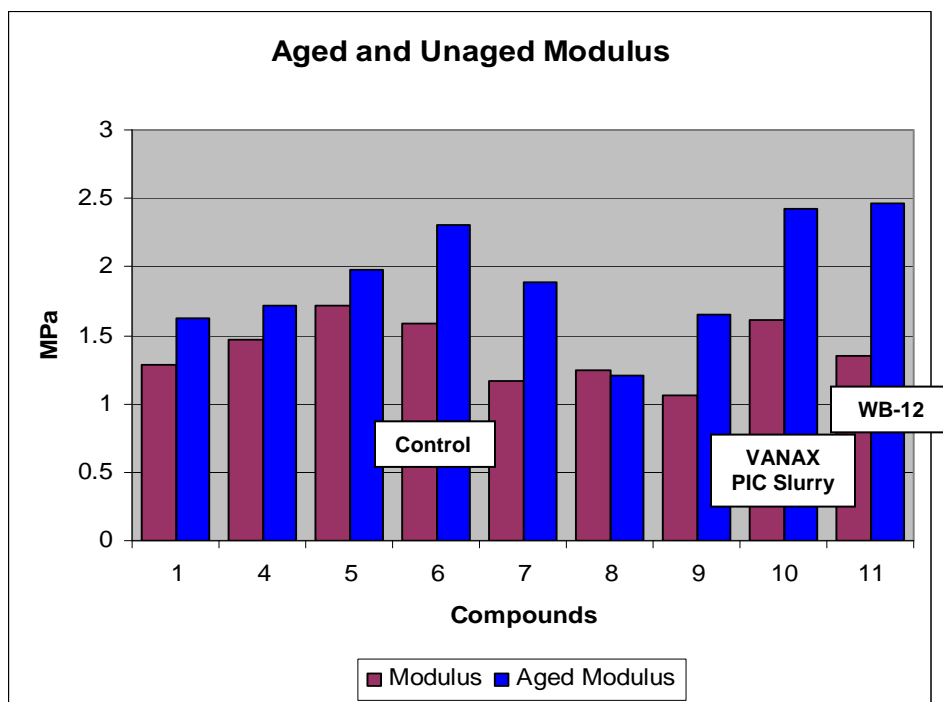


Figure 6: Aged and Unaged Modulus

To make things a little easier, Compounds 2 and 3 have been excluded from Figure 6 since they contain DPG. Comparing the rest of the data to the control, it is clear that Compounds 10 (VANAX PIC Slurry) and 11 (WB-12) are very similar to Compound 6 in both aged and unaged modulus. Of note are Compounds 4 and 5, which contain DPTU alone. It appears that the DPG contributes little to the modulus of the finished material.

## Conclusion

This paper has looked at several potential replacements for diphenylguanidine in Neoprene. Based on the results, WB-12 provides the most equivalent properties, including tensile, modulus, and maximum torque. VANAX PIC Slurry is an excellent choice if one desires to improve the state of cure, since this accelerator offers similar tensile and modulus to the control and a higher maximum torque.

Determining a replacement cure system is not a simple task. It is important to look at all the different performance metrics and to select the one that best fits the requirements.

<sup>1</sup> European Chemicals Agency. About REACH. Retrieved from [http://guidance.echa.europa.eu/about\\_reach\\_en.htm](http://guidance.echa.europa.eu/about_reach_en.htm).

<sup>2</sup> Fitch, J.C. (1987). Polychloroprene Latexes. In R. Mausser (ed.), *The Vanderbilt Latex Handbook* (3rd ed.) (50-59). Connecticut: R.T. Vanderbilt Company, Inc.

<sup>3</sup> Layer, R.W. (1990). Introduction to Rubber Compounding. In R. Ohm (ed.), *The Vanderbilt Rubber Handbook* (13th ed.) (11-21). Connecticut: R.T. Vanderbilt Company, Inc.

<sup>4</sup> Carl, John C. (1962). *Neoprene Latex*. Delaware: E.I. Du Pont de Nemours & Company, Inc.

<sup>5</sup> DuPont Performance Elastomers. (2005). Basic Compounding of Neoprene Liquid Dispersion.

<sup>6</sup> Del Vecchio, R.J. (2001). Physical Testing of Rubber. In K. Baranwal and H. Stephens (eds.), *Basic Elastomer Technology* (208-234). Maryland: United Book Press.

<sup>7</sup> Del Vecchio, R.J. (ed). (2003). Glossary. *Fundamentals of Rubber Technology* (330). North Carolina: Technical Consulting Services.

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