

## Latex Growth

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### Synopsis

A method is described for preparing a latex with a particle size larger than can be obtained by direct emulsion polymerization. It consists in growing latex particles to larger size by feeding more monomer and adjusting the emulsifier concentration in a manner which prevents both coagulation and the formation of new micelles.

### INTRODUCTION

It is sometimes desirable to obtain a latex with a particle size larger than can be obtained by direct emulsion polymerization and smaller than can conveniently be made with suspension polymerization techniques.

Latex particles can be grown to several times their original diameter by means of a more elaborate multiple reseeded technique.<sup>1,2</sup>

The purpose of this investigation was to develop a technique for growing latex particles to larger sizes than can be obtained by direct emulsion polymerization.

### THEORY

Emulsion polymerization as understood today is largely based on the work done by Harkins and his co-workers during World War II (publication dates from 1947).<sup>3</sup>

Emulsifier molecules are usually long aliphatic and hence hydrophobic chains terminated by an ionizable and hence hydrophilic group. When these molecules are dissolved in water they tend to cluster together and form micelles. In a micelle the hydrophobic parts are at the interior of the micelle while the hydrophilic group faces the outside, in this case the water.

A certain finite concentration of emulsifier is necessary for micelles to form. This is called the critical micelle concentration. Below this concentration only individual emulsifier molecules exist. Above it, micelles exist in equilibrium with the individual molecules. The surface tension of an emulsifier solution drops rapidly with concentration, until at the critical micelle concentration it levels out to a steady value (Fig. 1).

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When a monomer which is only slightly water-soluble is added to the emulsifier solution, some of the monomer enters the micelles. The rest of the monomer is dispersed in small droplets which are fewer in number but larger in size. Harkins and others<sup>2-5</sup> have definitely proven that the micelle is the main locus of polymerization and hence of latex-particle formation. Therefore, in the growing of a latex to a larger uniform particle size it is important that the formation of new micelles be avoided, but extra emulsifier will have to be added to protect the larger particles.

The technique used consists in the continuous feeding of fresh monomer to a seed latex in the presence of catalyst. At all times the growing latex particles should be kept coated with an adequate soap layer to avoid coagulation. At the same time the soap concentration should never be so high as to generate new soap micelles which in turn would cause a second crop of latex particles.

### Optimum Surface Tension

In Figures 1 and 2 we have plotted the corrected surface tensions for soaps in water alone and in the presence of a polyvinyltoluene latex. The recipe for the preparation of this latex is described in the experimental section (experiment A). It is a fairly uniform latex with an average particle size of 1420 Å. Figures 1 and 2 present the same data, with the following difference: in Figure 1 the soap concentration is plotted linearly and in Figure 2 logarithmically. One sees especially in Figure 1 or Table I that in pure water the surface tension drops very quickly to a level below 30 dyne/cm. The soap concentration at which this level is reached is called the critical micelle concentration (CMC). After the CMC is reached, any added soap molecules aggregate into micelles. The micelles can absorb free monomer and thus cause the formation of latex particles. The formation of

TABLE I  
Surface Tension  $\gamma$  of Soap in Water Solution

Active surfactant concentration, % <sup>a</sup>	$\gamma$ , dyne/cm.	
	$\gamma_{app.}$	$\gamma_{corr.}$
2.507	28.3	25.0
1.491	28.3	25.0
0.850	29.2	25.9
0.372	30.4	25.9
0.234	30.9	27.6
0.136	31.4	27.8
0.058	36.0	32.5
0.000	69.6	65.0 <sup>b</sup>

<sup>a</sup> Aerosol OT (a product of the American Cyanamid Company) was used; active ingredient: dioctyl ester of sulfosuccinic acid.

<sup>b</sup> The water used was plant-deionized water, which contains some organic materials. This explains our figure, which is lower than found in the literature.

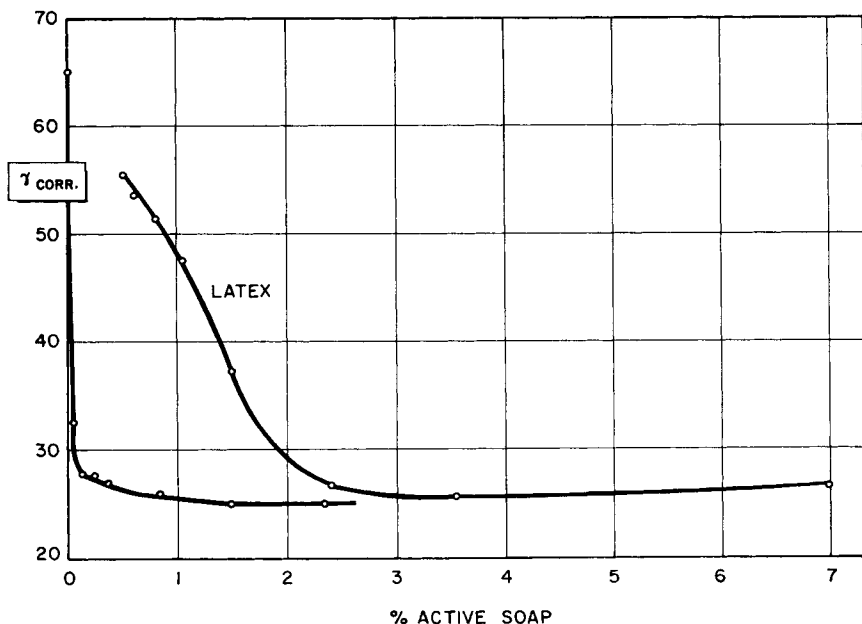


Fig. 1. Surface tension vs. soap concentration, with and without latex present.

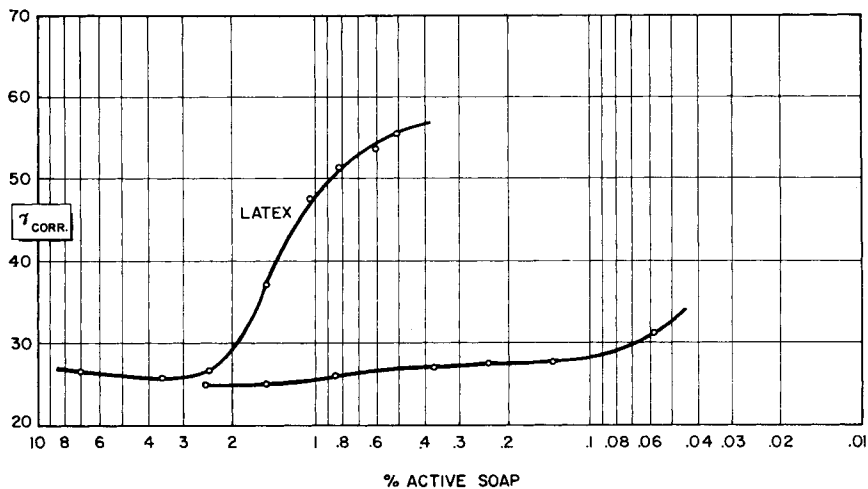


Fig. 2. Surface tension vs. soap concentration, with and without latex present.

new particles (second crop) should be avoided in a controlled growth-emulsion polymerization.

When latex is present, the surface tension does not drop at the same low soap concentration, because the soap molecules are adsorbed on the latex particles. Only when these are about completely covered does the surface tension drop to the micelle level. As can be seen in Figure 1 or 2 (or Table

II) a surface tension between 30 and 50 dyne/cm. represents the region where the particles are about completely covered and where no new micelles have yet been formed. This is the optimum region to work in during a growth-emulsion polymerization where we do not want coagulation (and therefore maximum soap coverage) or new micelles.

TABLE II  
Surface Tensions  $\gamma$  of Soap in Latex Solutions

Total active surfactant concentration, % <sup>a</sup>	Latex polymer solids, % <sup>b</sup>	$\gamma$ , dyne/cm.	
		$\gamma_{app.}$	$\gamma_{corr.}$
6.999	36.16	30.2	26.6
4.260	37.08	37.4 <sup>c</sup>	—
3.560	37.44	29.2	25.7
2.410	38.04	30.2	26.6
1.500	38.51	41.6	37.2
1.044	38.76	52.6	47.6
0.808	38.88	56.5	51.3
0.602	38.99	58.8	53.5
0.540	39.04	60.9	55.5

<sup>a</sup> Soap used in the polymerization of the latex as well as the soap added in this series of measurements. Monawet M050 was used during the polymerization, Aerosol OT for the measurements. Their active ingredient is the same: dioctyl ester of sodium sulfosuccinic acid.

<sup>b</sup> Polyvinyltoluene latex, particle size 1420 Å.

<sup>c</sup> High reading, caused by dried latex clinging to tensiometer ring.

In Table II we see that a 1.5% active soap concentration gives a corrected surface tension of 37.2 dyne/cm. in the presence of 38.51% polymer solids of polyvinyltoluene latex. Here follows an example of a surface-coverage calculation. In 100 g. of latex the number of particles was

$$N = 38.51 / [(\pi/6)(1420)^3 \times 10^{-24}]$$

and the surface of a single particle is  $s = \pi(1420)^2 \text{ Å}^2$ . The total surface in 100 g. of latex is then:

$$Ns = (38.51 \times 6/1420)10^{24} \text{ Å}^2 = 163 \times 10^{21} \text{ Å}^2$$

The amount of active soap is 1.5 g.; hence  $1.500/163 \approx 9.2$  mg. active Aerosol OT per  $10^{21} \text{ Å}^2$ .

Actually, most growth was attained at a level of 10 mg. active Aerosol OT/ $10^{21} \text{ Å}^2$  or 1 mg./ $10^{20} \text{ Å}^2$ . As can be seen on Figure 1 or 2, this slightly higher soap concentration would not bring the surface tension to a sufficiently low level at which new micelles would be formed.

### Total Surface

The importance of knowing the total surface (TS) of all the latex particles during growth of the latex at all times is obvious.

If  $\alpha$  is the amount of dry solid seed latex in grams and  $x$  is the amount of monomer added in grams, then the weight-growth ratio is  $(x + \alpha)/\alpha$ . If  $\phi_i$  is the initial diameter of the seed latex and  $\phi$  the diameter after addition of  $x$  grams of monomer, then the volume growth ratio would be  $(\phi/\phi_i)^3$ . We may write

$$(\phi/\phi_i)^3 = (x + \alpha)/\alpha$$

and the diameter is

$$\phi = \phi_i[(x + \alpha)/\alpha]^{1/3} \quad (1)$$

The volume and weight (if polymer density  $\approx 1$ ) of the seed latex particle is  $(\pi/6)\phi_i^3$ . The number of particles at the beginning—and throughout the reaction, if correctly run—is then  $6\alpha/\pi\phi_i^3$ , where  $\phi_i$  is expressed in centimeters. The surface of a single latex particle at any time during the growth will be equal to  $\pi\phi^2$ . Therefore, the total surface at all times will be:

$$\text{TS} = (6\alpha/\pi\phi_i^3)\pi\phi^2$$

or, from eq. (1)

$$\begin{aligned} \text{TS} &= (6\alpha/\phi_i^3) \phi_i^2[(x + \alpha)/\alpha]^{2/3} \\ &= 6\alpha/\phi_i[(x + \alpha)/\alpha]^{2/3} \end{aligned} \quad (2)$$

This shows that the total surface will increase roughly as the two-thirds power of the monomer feed because  $\alpha$  usually is very small compared to  $x$ , especially in the hundredfold volume growth experiments we performed.

### Final Surface Tension

As can be seen in the experimental section, the final surface tension at the end of the growth experiment is always higher than it ought to be in accordance with our theory. An explanation may be found in the Gibbs-Thomson relation:

$$\ln(S_r/S) = 2\sigma M/dRT r$$

where  $S_r$  = escaping tendency of emulsifier molecule from surface of radius  $r$ ,  $S$  = escaping tendency from flat surface,  $\sigma$  = interfacial tension,  $M$  = molecular weight of emulsifier,  $d$  = density of emulsifier at the surface,  $R$  = gas constant, and  $T$  = absolute temperature.

Qualitatively, this means that an emulsifier molecule is more tightly bound by a flatter surface. When the latex particles grow, their radius  $r$  increases, and their surface becomes flatter. This may explain why there is less free soap in the water phase and hence a higher surface tension.

The critical micelle concentration can be estimated<sup>6</sup> by plotting the results of several soap titrations at different latex dilutions and extrapolating to zero polymer concentration. When this method is applied to latices of different size but with the same soap, the larger size latices invariably ex-

trapolate to a lower critical micelle concentration<sup>1</sup> than the smaller ones. We believe that the Gibbs-Thomson equation clarifies this anomaly also. The larger-size latex binds the soap more strongly so that on extrapolation less soap appears to be free.

### APPLICATION

A seed latex with a particle size of 1420 A. ( $=\phi_i$ ) was prepared; 5 ml. of this 40% solid seed latex were used, i.e.,  $\alpha = 2$ .

When this information is inserted into eq. (2) we find:

$$\begin{aligned} \text{TS} &= [(6)(2)/1420](1/2)^{2/3}(x+2)^{2/3}10^{24} \text{ A.}^2 \\ &= (6/1420)2^{1/3}(x+2)^{2/3}10^{24} \text{ A.}^2 \\ &= 5.32(x+2)^{2/3}10^{21} \text{ A.}^2 \end{aligned}$$

Similarly:

$$\phi = \phi_i[(x+2)/2]^{1/3}$$

When we calculate this information for several  $x$  values (in grams) we find the values given in Table III.

TABLE III

$x$	$x+2$	$(x+2)^{2/3}$	TS, $\text{A.}^2 \times 10^{21}$	Wt. active soap required, mg.	Wt. OT 75% required, g.	Wt. 75% used, g.	$\phi$ , A.
0	2	1.59	8.46	846			1420
8	10	4.64	24.7	247	See text		2430
18	20	7.37	39.2	392			3060
48	50	13.60	72.3	723	0.96	0.50	4150
98	100	21.50	114.7	1147	1.53	1.50	5235
148	150	28.25	150.3	1503	2.03	2.00	6000
198	200	34.20	182.0	1820	2.43	2.50	6600

The weights of soap required are based on 1 mg./10<sup>20</sup> A.<sup>2</sup> as calculated earlier. The soap used was the dioctyl ester of sodium sulfosuccinate in the commercial form of Aerosol OT 75% active, a product of the American Cyanamid Company. The weight of OT required was then calculated.

The addition of soap is not linear, but exponential. This was done by using three different soap-in-monomer solutions for the feed. We actually used in the first 48 (or 50) g. addition about half of the soap necessary and made up for it in the second addition (see experimental section). We felt free to do this, because during the first addition the solids content is so low that the consequent lack of much danger of coagulation enables one to drip in the soap-in-monomer solution at a faster rate. The amount of soap introduced together with the seed latex is very small and was ignored. The

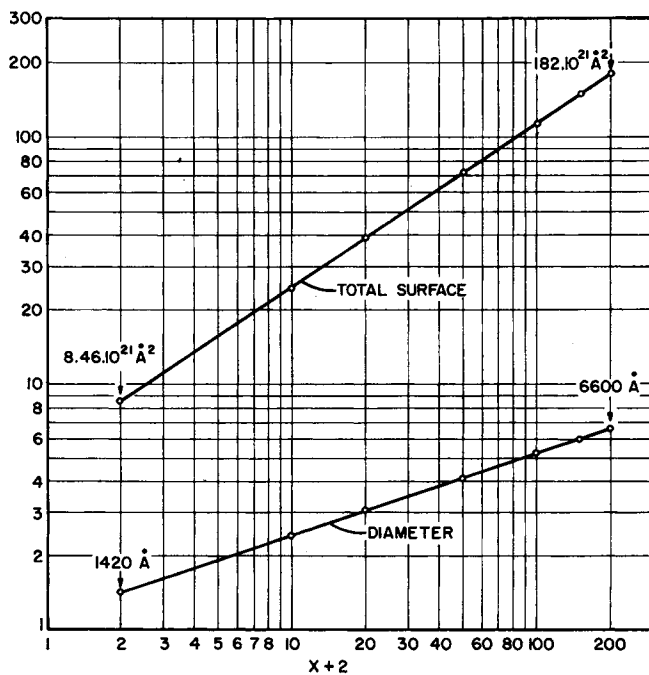


Fig. 3. Total surface and diameter of latex particles as a function of monomer feed.

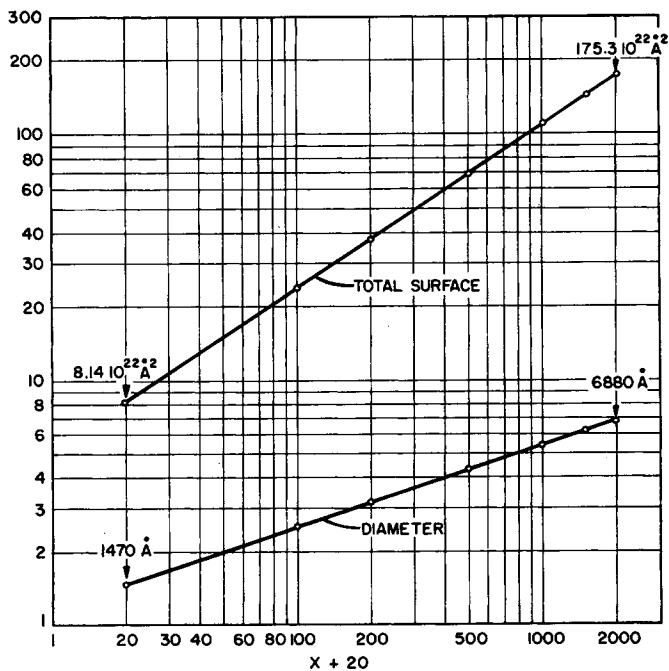


Fig. 4. Total surface and diameter of latex particles as a function of monomer feed.

final particle size was 6620 A. after an addition of 200 g. of monomer ( $x + 2 = 202$ ). By use of eq. (1), a diameter of 6613 A. was predicted. Figure 3 is a semilogarithmic plot of diameter and total surface as a function of the monomer feed  $x$  plus the seed latex solids  $\alpha$ .

In another experiment a similar growth polymerization was performed on a larger scale. A seed latex ( $\phi_i = 1470$  A.) was grown continuously to 7260 A. Details are described in the experimental section (C and D). The results of the calculations are shown in Table IV (see also Fig. 4).

TABLE IV

$x$	$x + 20$	$(x + 20)^{2/3}$	TS, A. <sup>2</sup> $\times 10^{22}$	Wt. of active soap required, mg.	Wt. OT 75% required, g.	Wt. OT 75% used, g.	$\phi$ , A.
0	20	7.35	8.14				1470
80	100	21.50	23.82		See text		2514
180	200	34.10	37.78				3165
480	500	62.80	69.59	6.96	9.28	5	4295
980	1000	100.00	110.82	11.08	14.77	14	5415
1480	1500	130.60	144.73	14.47	19.30	19	6200
1980	2000	158.20	175.31	17.53	23.37	24	6820

The final latex had a diameter of 7260 compared to a predicted value of 6820 A., probably because the seed latex was not accurately weighed out in this experiment, but was added by volume.

## EXPERIMENTAL

### Experiment A: Initial Seed Latex for Growth Experiment

The latex was made in washed citrate bottles according to the following recipe: Monowet M050, 2 g.;  $K_2S_2O_8$  (5% aqueous solution), 10 ml.; deionized water to give 150 g.; vinyltoluene (no inhibitor), 100 g. After purging with  $N_2$  the bottles were placed in a tumbler bath (12 rpm) for 2 $\frac{1}{2}$  hr. at 70°C. and  $\frac{1}{2}$  hr. at 75°C. The latex was filtered following a slow cooling over a 1-hr. period; pH = 2.7-2.8; P.S. = 1420 A., % solids = 39.7; conversion = 97.8%; polymer solids = 39.1%.

### Experiment B: Growing Particle Size of Seed Latex 100 Volumes

The following were placed in a 1000-ml. flask fitted with an addition funnel and a stirrer: deionized water, 275 ml.;  $K_2S_2O_8$  (5% aqueous solution), 10 ml.; latex from experiment A above, 5 ml. (2 g. solids).

Following a  $N_2$  purging the sample was heated to 70°C. in a bath. The prepurged additions listed below were made dropwise at 70°C.: over 1 hr., 50 g. vinyltoluene, 0.5 g. Aerosol OT 75%; over 1 hr. 50 g. vinyltoluene, 1.0 g. Aerosol OT 75%; then 10 ml.  $K_2S_2O_8$  (5% aqueous solution); and



over 2 hr. 100 g. vinyltoluene, 1 g. Aerosol OT 75%. All monomer added had been flash-distilled to remove inhibitor. The temperature was maintained at 70°C for an additional 2 hr. after the last of the monomer was added. The product had solids = 39.4%; conversion 98.6%; final surface tension (S.T.) = 53.7 dyne/cm. (apparent). The final size of the particles in the latex was calculated to be 6613 Å. The average particle size as measured by the electron microscope was 6620 Å. with no second crop.

### **Experiment C: Pilot-Plant Continuous Feed Seed Latex For Growth Experiments**

The following is the recipe of a pilot-plant run made at a temperature of 70°C. and under agitation of 60 rpm: H<sub>2</sub>O (condensate), 58 lb.; Aerosol OT 75%, 50 g. in 2 lb. H<sub>2</sub>O. The water phase was then heated to 70°C. while purging with N<sub>2</sub> was continued. The following were introduced into the reactor during the heating: vinyltoluene, 10 lb. at 50°C.; K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (dry), 30 g. at 70°C. The 10-lb. addition of monomer was allowed to react for about 1/2 hr. Then a continuous feeding of monomer and surfactant dissolved together began. The rate of feeding was 1/4 lb./min. for 2 hr. The following quantities were added in the manner described: vinyltoluene, 30 lb.; Aerosol OT 75%, 250 g. During the reaction the latex received: K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (dry), 40 g., of which 10 g. was added before beginning continuous feeding and 10-g. portions after 10, 20, and 30 lb. of the continuous feed had been introduced. When monomer addition was complete, the temperature was raised to 85°C. for 1/3 hr. The particle size was 1470 Å., solids were 38.8%, and residual monomer was 0.24%.

### **Experiment D: Growing Pilot-Plant Seed Latex in 12-Liter Flask Over 100 Volumes**

A 12-liter flask fitted with a vented addition, a stirrer, a thermowell, and an entrance for wafting gas received the following: deionized water, 2750 ml.; K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (5% solution), 100 ml.; latex from experiment C, (37.4% polymer solids), 53.5 ml. (20 g. solids). The monomer used in this experiment was flash-distilled to remove inhibitor. The monomer together with dissolved surfactant was added dropwise in the following prepurged increments: vinyltoluene, 480 g., and Aerosol OT 75%, 5 g.; then vinyltoluene, 500 g., Aerosol OT 75%, 9 g., and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (5% solution), 100 ml. (two 20-ml. shots during reaction); then vinyltoluene, 1000 g., Aerosol OT 75%, 10 g., and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (5% solution), 100 ml. (after all monomer was added).

The monomer was added over a 12-hr. period at 70–85°C., and when the addition was complete the temperature was raised to 90°C. and maintained for 2 hrs. The reaction mixture was then slowly cooled in air. During and after the cooling we added Aerosol OT 75/100%, 400 ml. Final surface tension was 52 dyne/cm. There was some unidentified sludge. Latex solids = 31.6%. The final particle size was 7260 Å. No new particles were found under the electron microscope.

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### Résumé

On décrit une méthode de préparation d'un latex composé de particules plus grandes que celles obtenues par polymérisation directe en émulsion. Ce procédé consiste à faire croître les particules de latex jusqu'à une dimension plus grande en ajoutant d'avantage du monomère et en ajustant la concentration en émulsifiant de façon à empêcher la coagulation et la formation de nouvelles micelles.

### Zusammenfassung

Es wird eine Methode zur Darstellung eines Latex mit grössern Partikeln als man durch direkte Emulsionspolymersation erhalten kann, beschrieben. Durch Zugabe von mehr Monomerem und Einstellung der Emulgatorkonzentration auf einen Wert, der sowohl Koagulation als auch Bildung neuer Mizellen verhindert, wird ein Anwachsen der Latexpartikel erreicht.

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