Nano-Particle Reinforced Latex Dispersions With Modified Colloidal Silica

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The impact of adding epoxysilane-modified colloidal silica to water-based coating formulations on the mechanical properties of resin films was studied. In general, the effect of the silica particles depended strongly on the resin and other components of the coating formulation but very significant improvements of hardness could be observed. The effect on the abrasion resistance of the coatings was less clear but still noticeable in many coating systems. Also, the modification ensures good compatibility with the resins and that the aesthetic properties of the coating (gloss and haze) are not compromised.

Addition of silica particles to waterborne wood lacquers enhances the grain structure in a manner similar to solventborne lacquers.

INTRODUCTION

In the past, there have been numerous investigations on the use of silica nano-particles in resin-based systems. Water-free systems of silane-modified colloidal silica particles have been found to enhance the mechanical properties of coatings.[1,2] Silane-modified fumed silica has been used to enhance coating properties.[3] Organosols have been used to improve scratch resistance in clear coatings by surface enrichment.[4] Aqueous colloidal silica has been utilized in copolymerization of resins,[5] and copolymerized colloidal silica resin hybrids are also used to enhance a variety of coatings properties like hardness, anti-blocking, and reduced dirt-pickup.[6] Silica particles made from TEOS have recently been investigated in copolymerization of hybrid coatings where hardness and adhesion properties were found to be improved.[7] Non-surface modified colloidal silica has been tested as a nano-filler in latex coatings with encouraging results concerning mechanical properties.[8] However, there have been very few studies done on the use of silane-modified water-based colloidal silica used in formulations of waterborne coatings.

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Recently, there has been great interest in such particles in waterborne lacquers since they often provide benefits like anti-blocking and "anfeuerung" in acrylic emulsion-based wood coatings. It is also very desirable to improve mechanical properties, such as hardness and abrasion resistance, of coatings. To this end, highly crosslinked systems like two-pack, or 2-k, systems are often required. Addition of colloidal silica dispersions to waterborne lacquers provides coatings with excellent mechanical properties.

Concentrated epoxysilane-modified colloidal silica in the form of aqueous sols is one of the most readily available sources of nano-particles for the coating area. Such sols are characterized by high solids content, up to at least 50% by weight of silica depending on particle size, which ranges from about 5 to 100 nm. Compared with conventional silica sols, silane-modified colloidal silica provides greater stability towards aggregation and gelling, both as is and in latex-based coating formulations.[9-11]

Finally, from an environmental point of view, it is advantageous to use colloidal silica in latex-based coating formulations. Less resin will be needed as it is partially replaced by silica, with accompanying lower amounts of VOC. Softer resins can be used since silica addition will improve their mechanical properties to the level of those of harder resins, obviating the use of potentially hazardous film-forming agents such as NMP or glycol ethers.

EXPERIMENTAL

2-K Systems

The varnish formulations are detailed in *Tables* 1 to 8. Product weights are given in grams. The varnishes were applied by means of an applicator on aluminum substrates at dry film thicknesses between 40 and 50 µm. Persoz hardnesses were measured after the following drying times: 1 day, 7 days, 2 weeks, and 1 month at ambient temperature. Gloss measurements were performed after 30 days of drying. Before testing, all the samples were conditioned at 23°C and 50% RH during 24 hours. The resistances to abrasion were also determined by means of a Taber abraser after 30 days of drying at ambient temperature. The addition of colloidal silica was 0, 10, and 20% by weight calculated as dry silica based on dry resin.

Materials

RESINS: The resins used are shown in *Table* 9.

HARDENERS: Hardeners used included:

- Rhodocoat X EZ-D401 (a water-dispersible aliphatic polyisocyanate)
- Rhodocoat X EZ-M501 (a water-dispersible aliphatic polyisocyanate; more hydrophobic than Rhodocoat X EZ-D401)

SILICA: Silane-modified colloidal silica dispersion: Bindzil® CC30; epoxy silane-modified colloidal silica, 1.40 GPTMS/nm² colloidal silica surface, pH 7, particle size: 7 nm, silica content 30 wt%.

Lacquer Formulations—Two-Pack Systems

Lacquer formulations for the two-pack systems are shown in *Tables* 1–8.

Gloss and Haze

Gloss (20°) was measured of coatings applied on aluminum plates after 30 days of drying at ambient temperature. Haze index, defined as a gloss difference, was calculated from gloss measurements at 20° and 60° following ASTM D 4039 test (reflection haze of high-gloss surfaces).

Hardness—Persoz Hardness

The hardness of the different varnishes was determined by means of a "Persoz pendulum" according to ASTM D 4366. The gloss of the varnishes was determined as the average of five measurements.

Abrasion Resistance—Taber Abrasion

The resistance to abrasion of the different varnishes with and without addition of epoxy silane-modified colloidal silica applied on aluminum plates was determined by means of a Taber abraser following ASTM D 4060. The test was performed after 30 days of drying at ambient temperature. An abrasive wheel, CS17, under 1 kg load was used. The weight loss of the samples was measured after 100, 500, and 1000 revolutions. The weight loss was determined as the average of two measurements. In some cases, the test was stopped before 1000 revolutions were reached due to delamination of the films or due to local substrate baring.

RESULTS AND DISCUSSION

Compatibility—Gloss and Haze

The results of gloss and haze measurements are given in *Tables* 10 and 11. These results are very depending on the resin used. For two of the resins, No. 2 and No. 3, there is a big decrease in gloss when silica nanoparticles are added to the resin. For the other resins, there is little or no change in gloss or even an increase

Table 1—Formulation for Resin No. 1

Resin No. 1	Reference	10% SiO_2	20% SiO_2
C1 Setalux 6741	100	100	100
Dowanol PnB	2.81	2.81	2.81
Dowanol DPM	2.81	2.81	2.81
TINSTAB BL 277 (1% ds Solvesso 100)	1.00	1.00	1.00
Bindzil CC30	0	14.83	29.66
C2 Rhodocoat X F7-D401	21.85	21.85	21.85

Table 2—Formulation for Resin No. 2

Resin No. 2	Reference	10% SiO_2	20% SiO_2
C1 Setalux 6756	100	100	100
Dowanol PnB	1.96	1.96	1.96
Dowanol DPM	1.96	1.96	1.96
TINSTAB BL 277 (1% ds Solvesso 100)	1.00	1.00	1.00
Bindzil CC30	0	13.79	27.58
C2 Rhodocoat X EZ-D401	20.33	20.33	20.33

Table 3—Formulation for Resin No. 3

Resin No. 3	Reference	10% SiO_2	20% SiO_2
C1 Setalux 6762	100	100	100
Butylglycol	9.19	9.19	9.19
Dowanol DPnB	3.34	3.34	3.34
Butyldiglycol	4.93	4.93	4.93
TINSTAB BL 277 (1% ds Solvesso 100)	1.00	1.00	1.00
Bindzil CC30	0	15.17	30.34
C2 Rhodocoat X F7-D401	22.36	22.36	22.36

Table 4—Formulation for Resin No. 4

Resin No. 4	Reference	10% SiO_2	20% SiO_2
C1 Setalux 6778	100	100	100
Dowanol DPnB	6.60	6.60	6.60
TINSTAB BL 277 (1% ds Solvesso 100)	1.00	1.00	1.00
Bindzil CC30	0	15.17	30.34
C2 Rhodocoat X EZ-D401	22.36	22.36	22.36

Table 5—Formulation for Resin No. 5

Resin No. 5	Reference	10% SiO_2	20% SiO_2
C1 Setalux 6510	100	100	100
Solvesso 100	2.14	2.14	2.14
Butyl acetate	5.19	5.19	5.19
Butyl glycol acetate	4.66	4.66	4.66
TINSTAB BL 277 (1% ds Solvesso 100)	1.00	1.00	1.00
Bindzil CC30	0	14.48	28.96
C2 Rhodocoat X EZ-D401	43.17	43.17	43.17

Table 6—Formulation for Resin No. 6

Resin No. 6	Reference	10% SiO_2	20% SiO_2
C1 Setalux 6511	100	100	100
Butylglycol	1.96	1.96	1.96
Butyl acetate	2.83	2.83	2.83
Butyl glycol acetate	0.84	0.84	0.84
TINSTAB BL 277 (1% ds Solvesso 100)	1.00	1.00	1.00
Bindzil CC30	0	16.21	32.42
C2 Rhodocoat X EZ-D401	48.09	48.09	48.09

Table 7—Formulation for Resin No. 7

Resin No. 7	Reference	10% SiO_2	20% SiO_2
C1 Neocac E-180	100	100	100
Butyldiglycol	8.00	8.00	8.00
TINSTAB BL 277 (1% ds Solvesso 100)	1.00	1.00	1.00
Bindzil CC30	0	11.38	22.76
C2 Rhodocoat X EZ-M501	45.92	45.92	45.92

Table 8—Formulation for Resin No. 8

Resin No. 8	Reference	10% SiO_2	20% SiO_2
C1 Neorez R-2135	100	100	100
Dowanol DPnB	6.00	6.00	6.00
TINSTAB BL 277 (1% ds Solvesso 100)	1.00	1.00	1.00
Bindzil CC30	0	12.07	24.14
C2 Rhodocoat X EZ-M501	48.7	48.7	48.7

Figure 1 -Persoz hardness in function of coating composition and drying time at ambient temperature.

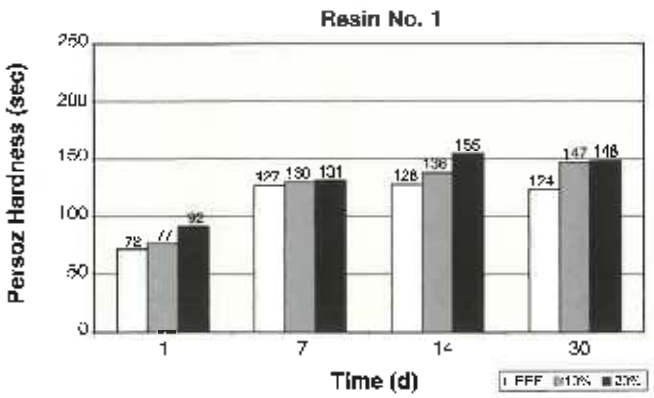


Figure 2---Persoz hardness in function of coating composition and drying time at ambient temperature.

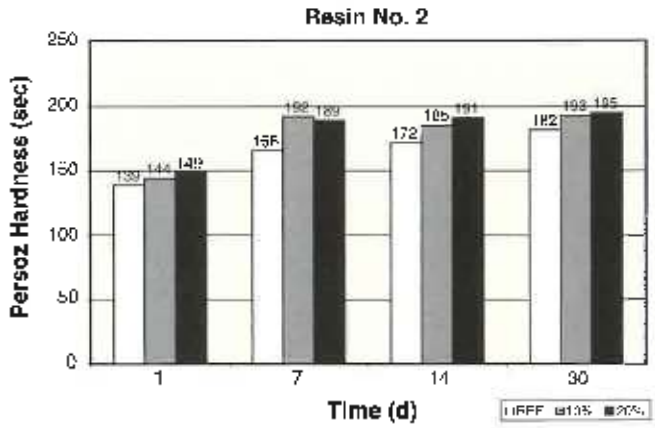


Figure 3 Persoz hardness in function of coating composition and drying time at ambient temperature.

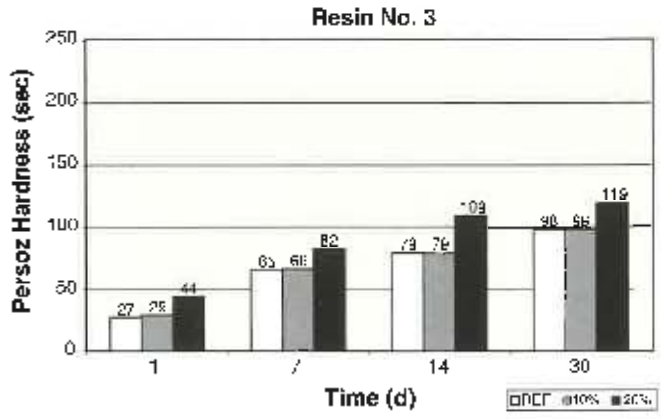


Figure 4—Persoz hardness in function of coating composition and drying time at ambient temperature.

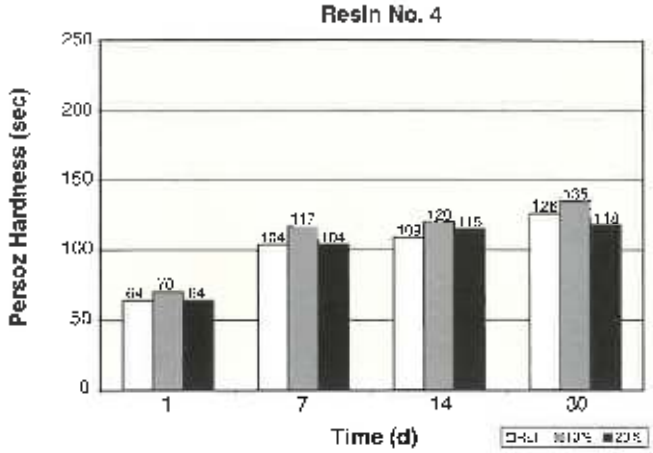


Figure 5—Persoz hardness in function of coating composition and drying time at ambient temperature.

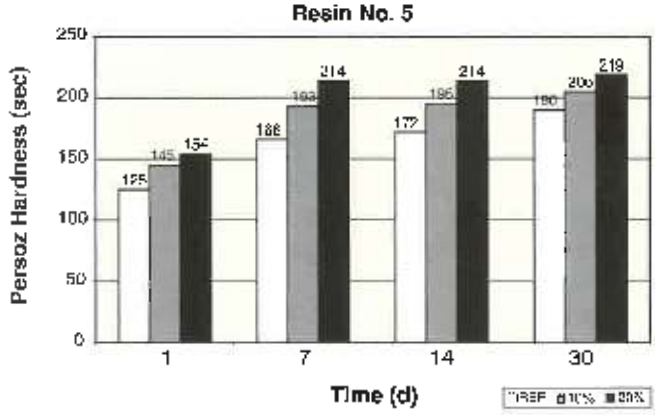


Figure 6—Persoz hardness in function of coating composition and drying time at ambient temperature.

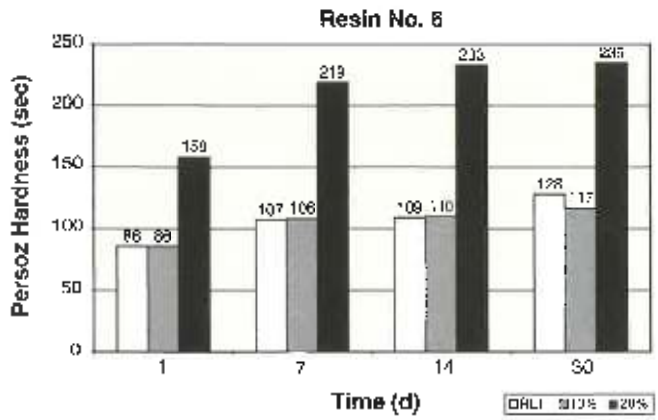


Figure 7—Persoz hardness in function of coating composition and drying time at ambient temperature.

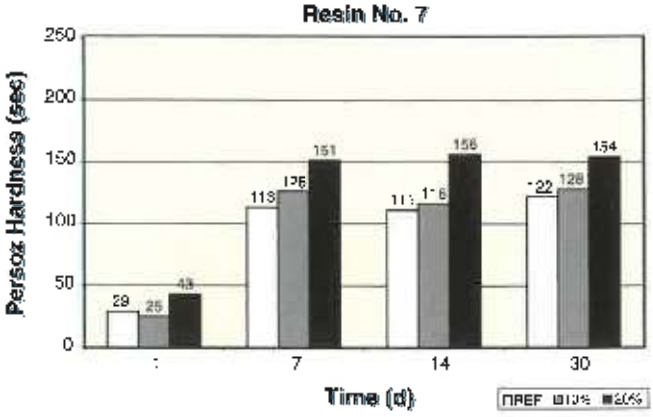
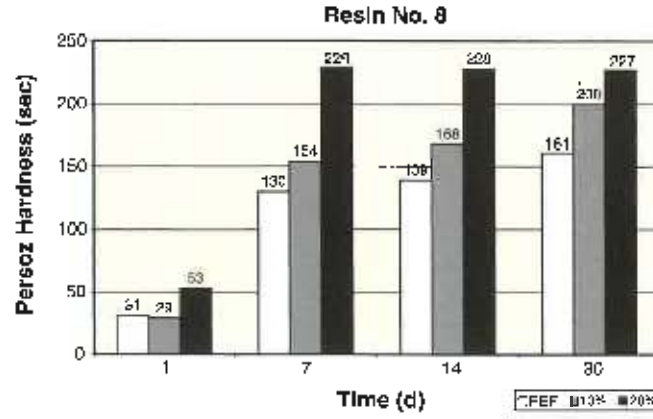


Figure 8—Persoz hardness in function of coating composition and drying time at ambient temperature.



in gloss upon silica addition, indicating good compatibility of the silica with the resin.

Hardness—Persoz Hardness

Evolution of hardness as a function of drying time and coating composition is presented for the different resins in *Figures* 1–8. The mean hardness values for each varnish are noted on the different graphs.

The effect of silica addition seems to be most pronounced for resins No. 5–8. For these resins, the effect of epoxysilane-modified colloidal silica is most pronounced for the 20 wt% silica addition to the resin (dry on dry). There is no proportionality between the amount of added inorganic particles and the property response. To achieve good improvement in hardness it is important to have good interaction/crosslinking between the resin and the silica particle, as well as to build a structure, like a skeleton, of silica in the resin matrix. In such cases it is possible to significantly improve the mechanical properties even at low silica additions.[12]

With the exception of resin No. 4, and in particular for resin No. 6, addition of 20 wt% of epoxysilane-modified silica improves the hardness of the coatings at all drying times studied. The increase in hardness was particularly noticeable at shorter drying times. Silica addition accelerates the development of the final hardness of the films, which is probably due to increased interactions/crosslinking between the components of the system, e.g., resin No. 8 with 20% silica addition will reach the ultimate hardness in seven days instead of 28 days.

The surface of the epoxysilane-modified silica particles contains diol groups, which can react/crosslink with carboxyl, hydroxyl, and isocyanate groups on the organic components of the system. Addition of silica to the acrylic binders 2 and 4 increases hardness considerably less than it does for the acrylic polyol binders 5 and 6. The polyol component of the latter type of binders contributes more reactive groups to the system than the pure acrylic binders 2 and 4. For resin No. 4, the hardness improvement is insignificant or nonexistent at all drying times at 20% addition of silica, whereas 10% addition causes a moderate increase of hardness. The seemingly inconsistent response of hardness to the amount of silica added may be due to aggregate formation. Above a certain critical concentra-

Table 9—Resins

Resin No.	Type	Solid Content (%)	pH	Note
1	Setalux 6741: Acrylic	43%	pH 8	
2	Setalux 6756: Acrylic	40%	pH 8	Surfactant free, self-crosslinking
3	Setalux 6762: Styrene-acrylic	44%	pH 8	
4	Setalux 6778: Acrylic	44%	pH 9	Gradient particle morphology, self-crosslinking
5	Setalux 6510: Acrylic polyol	42%	pH 8	Acid value: 7.8 –9.9 mg KOH/g
6	Setalux 6511: Acrylic polyol	47%	pH 8	Acid value: 6.6 –8.5 mg KOH/g
7	NeoPac E-180: Acrylic-PU	33%	pH 8	Copolymer
8	NeoRez-2135: PU	35%	pH 8	Aliphatic PU dispersion

Figure 9—Resin No. 5 with 10% SiO_2.

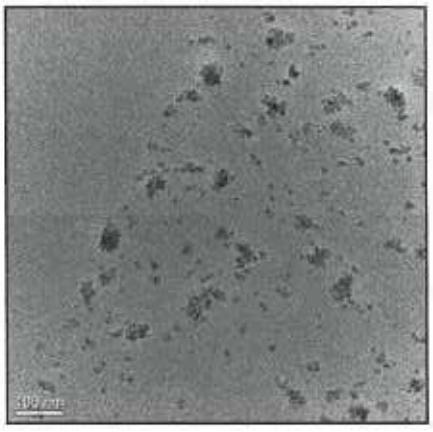


Figure 10—Resin No. 5 with 20% SiO_2.

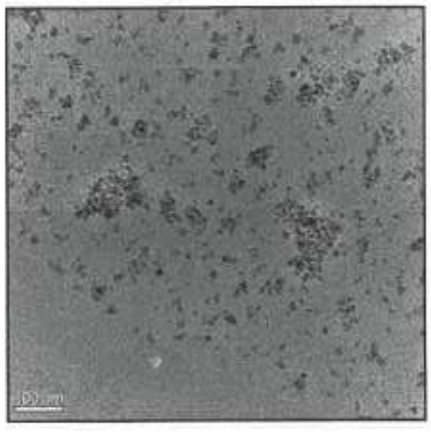


Figure 11—Resin No. 6 with 10% SiO_2.

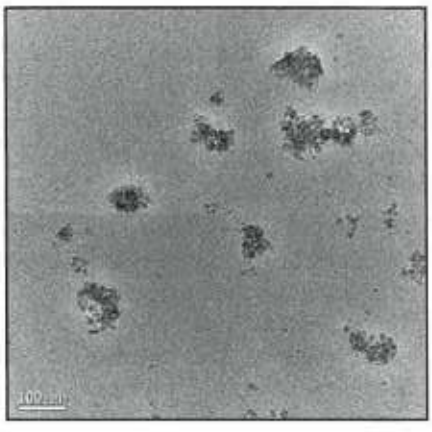


Figure 12—Resin No. 6 with 20% SiO_2.

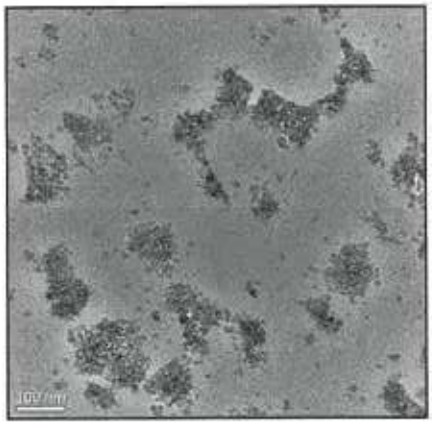
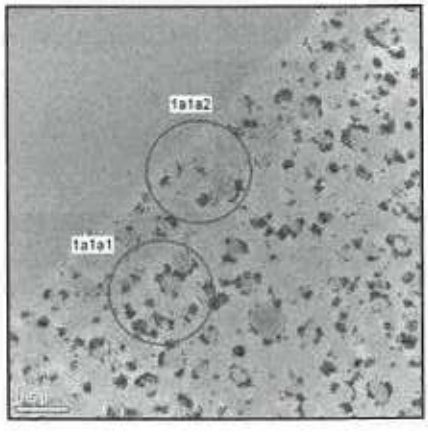


Figure 13—Resin No. 6 with 20% SiO_2.



lated or enriched at the binder–air interface. However, in contrast to the situation with resin No. 5, *Figures* 11–13 show that the silica particles have clustered around the droplets of the polyisocyanate hardener, perhaps preventing them from reacting effectively with the binder. There is no enhancement of the abrasion resistance at 10% and only modest improvement at 20% silica addition on resin, as might be expected from poor interaction between the silica and resin. On the other hand, the effect of the silica particles on the Persoz hardness while small or non-existent at 10%, is quite large at 20% addition of silica. The increase in hardness of the resin by the larger aggregates of silica particles at 20% silica addition may therefore be analogous to the observation that aggregation of nano-particles leads to increase in Young's modulus, especially by creating some occluded volumes in the matrix which augment the effective fraction of nano-filler.[11]

Anfeuerung—Enhancement of Grain Structure and "Anfeuerung" by Wood Lacquers

It has been reported in literature that colloidal silica in water based wood coatings comprising colloidal silica, organosilane, and latex emulsion can penetrate into the wood substrate.[12] As indicated in *Figure* 14, that addition of epoxysilane-modified 7 nm silica particles to waterborne one-pack coating formulations containing acrylic binders enhances and complements the wood grain structure by so-called "anfeuerung," giving an appearance similar to solvent-based coating systems. This valuable aesthetic effect can be expected to be present also with waterborne two-pack coating systems based on acrylic binders to which silica particles have been added, combined with the excellent mechanical properties characteristic of such systems.

Figure 14—1-K water-based lacquer formulated on resin No. 2 without (left) and with (right) 20% SiO_2 addition of epoxy-silane modified colloidal silica.

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