Water Repellent Treatment of Building Materials
Proceedings of Hydrophobe II
Zürich, September 1998, Aedificatio Publishers pp.21-36

Reactivity of Functionalised Silicon Compounds on Brick and Limestone

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Abstract

α,ω-diethoxy-polydimethylsiloxane was used to study the interaction of the functional groups on brick and limestone. Results of extraction experiments with acetone after treatment with the model compound revealed a chemical reaction between the ethoxy groups and reactive groups of the substrates.

Keywords: chemical reaction, ethoxy groups

1 Introduction

Reactive silicon compounds form the basis of many water repellents at present time[1]. Their ability to form Si-O-Si (siloxane) linkages through hydrolysis and subsequent condensation leads to the formation of a silicon based resin which imparts water repellency to the surface of the stone.

The study of water repellent agents for building materials has usually been evaluated in terms of the effectiveness in relation to the nature of the polymer, the concentration of the active ingredient, the type of solvent, etc...[2,3]. Less emphasis has been given to the type of interaction of the active ingredient on the stone objects, which should be part of the necessary parameters for a comprehensive evaluation of the effectiveness of a product. Based on the different behaviour of silanes and fluorinated polymers on different supports, Biscontin et al [4] concluded an interaction between the product and the support.

The directly evidence of the presence, the distribution and the chemical characteristics of a water repellent in building materials by FTIR is very difficult. Only for highly concentrated treatments, FTIR may be a valid technique for the identification of a water repellent. For applications similar to practice, the amount of water repellent is very low. If one takes into account for a consumption of 1000 g/m^2, a percentage dry weight of 8 %, an impregnation depth of 0.5 cm and a density of the substrate of 1.8 g/cm^3, a treated sample contains 0.9 w% of water repellent. This amount is lower than the detection limit of various FTIR techniques.

This paper describes the investigation on the reactivity of functionalised silicon based compounds on brick and limestone. The methodology is based on extraction experiments with aceton after treatment with a model compound : $\alpha\,\omega$-diethoxypolydimethylsiloxane with a degree of polymerisation (D.P.) of 15.

Bricks treated with Wacker 280 and Goldschmidt Tegosivin HL100 have also been extracted to follow up the chemical composition of the extract.

2 Experimental

2.1 Products

Goldschmidt MU1469, Goldschmidt Tegosivin HL100 and Wacker 280 were used to investigate the reactivity of functional groups towards different supports. HL100 consists of mono-, di- and tri-ethoxyfunctionalised silicon compounds. W280 contains ethylsilicate, trialkoxy functionalised silanes and condensation products of these.

The properties of the products are shown in table 1. The dry weight results from the evaporation of the diluent and, eventually, volatile compounds, and from the reaction of the reactive components.

The catalyst used for HL100 and MU1469 is a 50 w% solution of dibutyltindilaurate in white spirit (product/catalyst : 49/1 w/w).

Table 1: Chemical properties and dry weight of Goldschmidt MU1469, Goldschmidt Tegosivin HL100 and Wacker 280.

Brand name	Type of product	Type of reactive groups (b)	Type of hydrophobicf unctions (b)	Dry weight (%)
Goldschmidt MU1469 (a)	polymeric siloxane	OEt	Me-	95 (c)
Goldschmidt Tegosivin HL100	commercial water repellent (oligomeric siloxane)	-OEt	Me-	9 (d)
Wacker 280	commercial water repellent (oligomeric siloxane)	-OMe,-OEt	Me-, Oct-	6.5 (d)

(a) : this is not a water repellent but a product supplied by Goldschmidt for this investigatio

(b) : results from GC-MS and FTIR analysis

(c) : result after conditioning of MU1469 during 2 weeks

(d) : measured by weighing 0.5 g of a 10 % solution in white spirit in an aluminium cup followed by conditioning at 20 °C and 40 % relative humidity (R.H.) for 1 week.

2.2 Synthesis of linear polydimethylsiloxane

Linear polydimethylsiloxane is prepared by adding 87 mg of triethylamine to 5 g of MU1469. After stirring magnetically overnight, 2.04 g of trimethylethoxysilane as terminator is added. The solution is again stirred magnetically overnight. Polydimethylsiloxane is precipitated in n-hexane at -120°C. The obtained product is dried under vacuum. Figure 1 shows the FTIR analysis of MU1469 before (1) and after (2) the polycondensation reaction. After reaction, the absorption band at 954 cm^{-1} , characteristic for Si-OEt functions, has almost disappeared, while the intensity of the Si-O-Si band, at 1020 -1090 cm^{-1}, has increased, indicating a polycondensation between the reactive groups.

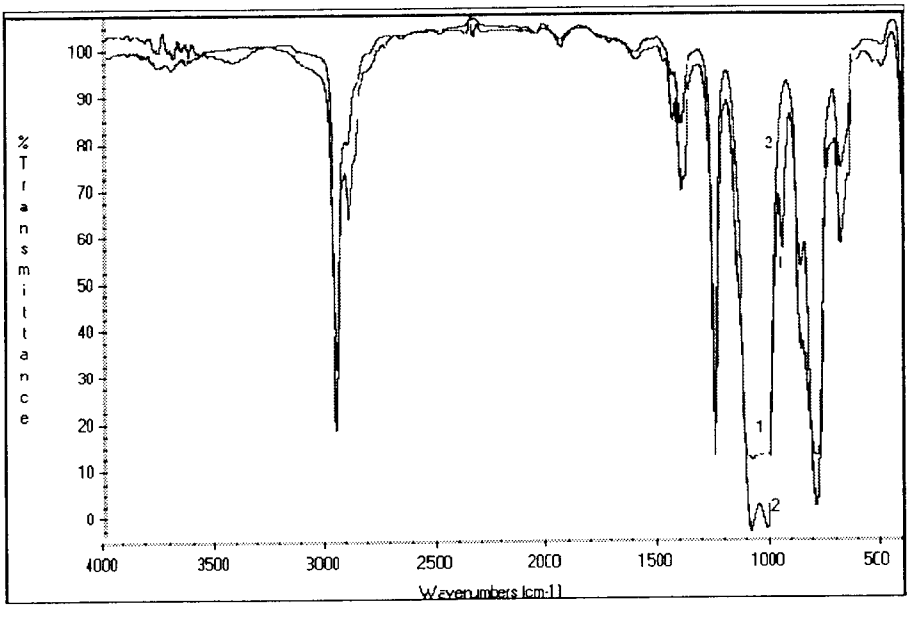

Figure 1: FTIR analysis of MU1469 before (1) and after (2) polycondensation

2.3 Brick and stones

One type of brick and three types of limestone were used to study the reaction between the reactive groups and the support. Their properties are shown in table 2:

Table 2: Hg-porosity and real density of brick, Euville, Gobertange and Massangis.

	Hg-porosity (%)	Real density (kg/m^3)
Brick	26-36	1544
Euville	10	2250
Gobertange	9.5	2400
Massangis	10	2240

2.4 Treatment and conditioning

Samples of 1 x 1 x 1 cm^3 are dried at 60°C till constant weight. The treatment is carried out by capillary absorption during 15 seconds.

Polydimethylsiloxane, synthesised as described in 2.2, is diluted with aceton till a solution of 50w% is obtained. After treatment, the samples are kept at 60 °C for 2 weeks

Tests with undiluted MU1469 have been carried out with and without addition of a catalyst. After treatment, the samples are conditioned at different temperatures for 2 weeks.

Samples treated with a 10 w% solution in white spirit of HL100 and W 280 are conditioned at 20 °C and 40 % R.H. for several weeks.

2.5 Extraction procedure

After conditioning at the set conditions, the samples are dried overnight at 60°C before the extraction procedure is started. The extractions are carried out with 30 ml of boiling aceton in a soxtec (TECATOR Soxtet System HT6) for 1 hour. After evaporation of the extraction solvent, the extract and the samples are dried at 60 °C till constant weight.

3 Results and discussion

3.1 Extractions of untreated samples

The extraction results of untreated brick and limestones are presented in table 3. From these results it can be concluded that under the experimental conditions aceton does not extract any soluble matter from untreated samples.

Table 3: Weight loss after extraction of untreated brick and limestones .

Substrate	Weight loss (%)
Brick	0.210
Euville	0.028
Gobertange	0.001
Massangis	0.019

3.2 Extraction of polydimethylsiloxane

Before investigating the reactivity of the functional groups of a silicon based water repellent, it is necessary to find out whether a non functionalised polysiloxane exerts interactions with the surface of a substrate.

For this, linear unfunctionalised polydimethyl siloxane, synthesised as described in 2.2, was used as treatment product. After conditioning, this product could be extracted completely from the brick. From this result, it can be concluded that there are no physical interactions between polydimethylsiloxane and the substrate.

3.3 Extraction of MU1469

Most common commercial water repellents contain crosslinking agents. After polycondensation, a crosslinked silicon resin is formed which is principally completely insoluble. Therefore, a systematic research has been carried out on the interaction of a reactive silicon compound with different substrates using ethoxy functionalised polydimethylsiloxane (MU1469). Since this product remains soluble after polycondensation reaction, the extraction results can be interpreted in terms of a reactivity of the reactive groups to the substrate.

Further, the question may rise whether the addition of a catalyst to the active ingredient is necessary to obtain an effective treatment. For this reason, a comparative investigation was done once without the addition of a catalyst and once in presence of a catalyst. For both studies, the influence of the temperature has been evaluated.

3.3.1 Without catalyst

Table 4 contains the remaining fraction of MU1469 on an inert substrate (aluminium),on brick and on several limestones after conditioning at different temperatures.

Table 4: Remaining fraction of MU1469 on aluminium, brick and limestones after conditioning for 2 weeks at different temperatures.

Temperature of conditioning (°C)	20	60	100
Aluminium	95	93	89
Brick	88	82	74
Euville	88	81	41
Gobertange	88	81	5
Massangis	86	78	22

The weight loss of MU1469 on an inert substrate results from the loss of volatile cyclic dimethylsiloxanes and oligomeric diethoxy functionalised dimethylsiloxanes. It was confirmed by GC-MS and FTIR analysis that a polycondensation hardly occurs between the reactive groups without adding a catalyst. The remaining fraction on brick and limestone is lower than on an inert substrate, indicating that even without catalyst, there can be a chemical reaction between the substrate and MU1469.

For temperatures up to 60 °C, the weight loss of MU1469 during conditioning is hardly influenced by the type of substrate. At 100 °C, the brick shows a remaining fraction of 74 %, while all tested limestones have lost more than 50 w% of the water repellent. This indicates that, especially for the Gobertange, these substrates contain compounds which are capable to degrade the silicon based water repellent.

Table 5 contains the extraction results, expressed as extracted fractions of the part which remains before the extraction (table 4).

These results show that, at 20 °C, the water repellent can be extracted almost completely from the Euville, indicating that under these circumstances the product exerts almost no chemical reaction with the substrate.

FTIR analysis of the extract (figure 2, spectrum 1) shows a signal at 954 cm^{-1} attributed to the presence of Si-OEt groupings. This signal is not present in the extracts from Massangis and Gobertange and in the extract from the treated Euville stone conditioned at higher temperatures. These results confirm the extraction results (table 5) , revealing a chemical reaction between the reactive groups of the polydimethylsiloxane and the substrate. This effect increases with increasing temperature of conditioning. At 100 °C, almost 90 % of the water repellent is chemically linked to the brick. For the

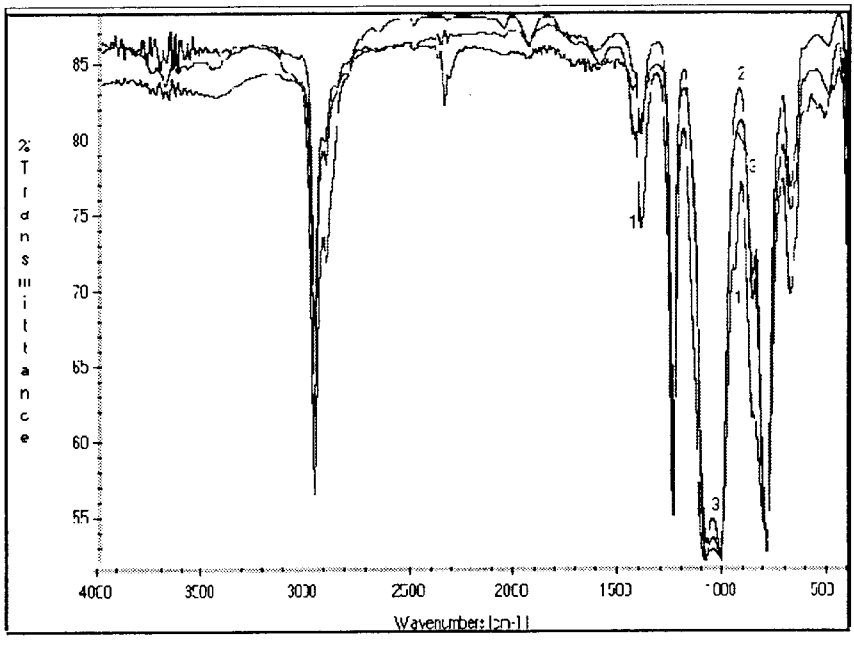

Figure 2: FTIR spectra of the extract from Euville treated with MU1469 after conditioning at 20 °C (1), 60 °C (2) and 100 °C (3).

Table 5: Extracted fractions of MU1469, expressed as extracted fractions of the remaining part before the extraction (table 4), from treated brick and limestones after conditioning at different temperatures.

Temperature of conditioning (°C)	20	60	100
Brick	79	*	11
Euville	95	48	21
Gobertange	39	6	100
Massangis	72	33	30

* : not determined

Gobertange only 39 % of MU1469 could be extracted after conditioning at 20 °C. At 60 °C, the weight extract decreases to 6 %. A conditioning at 100 °C results in a remaining fraction of MU1469 of 5 % (table 4) which is completely removed during the extraction procedure.

For all stones, the FTIR analysis of the extracts showed an increasing amount of low molecular weight dimethylsiloxane compounds with increasing temperature, which confirm previous described hypothesis of a degradation reaction.

3.3.2 With catalyst

Table 6 contains the dry weight of MU1469, to which a catalyst is added, on aluminium, on brick and on limestones conditioned at different temperatures.

These results show that only the brick and Euville stone show a dry weight of MU1469 comparable with that on the inert substrate, even at higher temperatures. For Gobertange and Massangis, lower remaining fractions are obtained at any temperature.

Except for the Gobertange conditioned at 20 °C, the remaining fraction of MU1469 is comparable with that obtained without catalyst. This indicates that, if there is a degradation procedure, it can be influenced by the catalyst in a way which depends on the type of substrate. For the Gobertange it favours the degradations at temperatures up to 60 °C. At 100 °C, al tested lime stones show higher dry weight values in case a catalyst is added. Under these circumstances the polycondensation and/or reaction with the subtrate is favoured.

In table 7, the extraction results obtained after conditioning at different temperatures are presented.

The results in table 7 reveal an increasing chemical reactivity between the reactive groups and the sub strate at increasing temperature. Similarly to

Table 6: Dry weight of MU1469+catalyst on aluminium, brick and limestones conditioned at different temperatures.

Temperature of conditioning (°C)	20	60	100
Aluminium	90	85	77
Brick	89	86	79
Euville	87	82	77
Gobertange	76	63	21
Massangis	84	76	63

Table 7: Extracted fractions of MU1469, expressed as extracted fractions of the remaining part before the extraction (table 6), from treated brick and limestones after conditioning at different temperatures.

Temperature of conditioning (°C)	20	60	100
Brick	30	19	13
Euville	96	63	13
Gobertange	29	18	12
Massangis	83	34	14

the results presented in table 5, this interaction depends on the type of material. A conditioning at 20 °C results in comparable extracted fractions for brick and Gobertange, while this fraction is remarkable higher for Euville and Massangis. A conditioning at 100 °C, results in extracted fractions between 12 and 14 % for all tested materials, indicating that almost 90 % of the remaining part before the extraction is chemically linked to the support.

3.4 Reactivity of MU1469 with glauconite

The lowest remaining fraction of MU1469+catalyst is found for Gobertange (table 6). The last contains glauconite, which is a potassium iron aluminosilicate [5,6]. The question rises whether the degradation of the functionalised polydimethylsiloxane compound can be activated by glauconite and, eventually, can be influenced by the presence of a catalyst. Therefore, glauconite powder has also been submitted to a similar treatment.

For this research, 1 g of glauconite powder was dried at 60 °C till constant weight. 0.5 g of MU1469 (+catalyst) is added to the powder, followed by conditioning at 20 °C and 40 % R.H. for 2 weeks. The remaining fractions of MU1469 on aluminium, glauconite and Gobertange, obtained once without and once with the addition of a catalyst, are presented in table 8.

The weight loss of MU1469 obtained on glauconite is lower than on aluminium and is hardly influenced by the presence of a catalyst. The lower remaining fraction indicates that this silicate provoces a chemical reaction of MU1469. The results for Gobertange differ from those of glauconite. Firstly, the weight loss is influenced by the presence of a catalyst, in such a way that a higher weight loss is obtained in case a catalyst is added to MU1469. Secondly, the dry weight obtained with MU1469 + catalyst on Gobertange is

Table 8: Remaining fraction of MU1469(+catalyst) on aluminium,glauconite and Gobertange after conditioning at 20 °C and 40 % RH.

	Produkt	
Substrate	MU1469	MU1469 + catalyst
Aluminium	95	90
Glauconite	87	85
Gobertange	88	76

even lower than that obtained on glauconite. Since the last is only a minor component of Gobertange (< 5 %), glauconite can not be the only component responsible for the higher weight loss.

3.5 Extractions of HL100 and W 280

The directly evidence of the presence and the distribution of a water repellent in building materials by FTIR is very difficult. Only for highly concentrated treatments, FTIR may be useful for the identification of a water repellent. For applications similar to practice, the amount of water repellent is very low. Therefore, an investigation has been carried out on the possibility to extract a water repellent from bricks, for which the treatment resembles an application in practice.

Figure 3 shows the FTIR spectra of the extracts of HL100 from bricks after several weeks of conditioning at 20 °C and 40 % R.H.. Figure 3 shows that 27 weeks after treatment, the extract is still representative for the product used and shows an absorption at 954 cm^{-1}, ascribed to the presence of SiOEt groupings. The last indicates that even after about 6 months, the polycondensation is still incomplete.

Figure 4 presents the results for W 280 after several weeks of conditioning. The extract obtained 2 weeks after treatment (spectrum 2) is representative for the product used. Similar results were obtained 13 weeks after treatment. After 19 weeks of conditioning, the Si-O-Si absorption signal at 1050 cm^{-1} can still be observed (spectrum 3), but with a low intensity. 27 weeks after treatment, the chemical structure of the extracted compound (spectrum 4) is no longer representative for the originally used product. Whether this is due to the characteristics of the product and/or a chemical degradation of the water repellent has not yet been revealed.

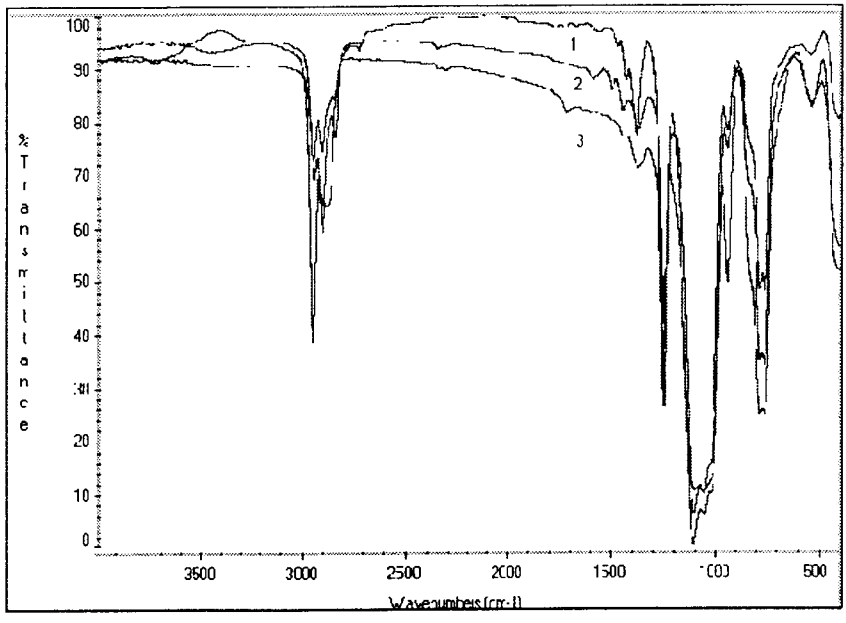

Figure 3: FTIR spectra of HL100 hardened in an aluminium cup (1), and of the HL100 extract from treated bricks after 2 (2) and 27 (3) weeks of conditioning (20°C, 40 % RH).

4 Conclusion

This report contains the results of an investigation on the possibility of an interaction between the reactive groups of a silicon based product and brick or limestone. The results are based on the extraction experiments with aceton after treatment with a model compound : Goldschmidt MU1469, containing mainly α,ω-diethoxy-polydimethylsiloxane with a polymerisation degree of 15, and with Goldschmidt Tegosivin HL100 and Wacker 280.

Unfunctionalised polydimethylsiloxane could be extracted for 100 %, indicating no interactions between polydimethylsiloxane and the brick surface.

The weight loss of MU1469 during conditioning is for all tested substrates higher than that on an inert substrate, concluding that there is a chemical reaction between the reactive model compound and the substrate.

All tested limestones showed at 100 °C lower remaining fractions than on brick, revealing a higher degradation of the compound. Except for Eu-

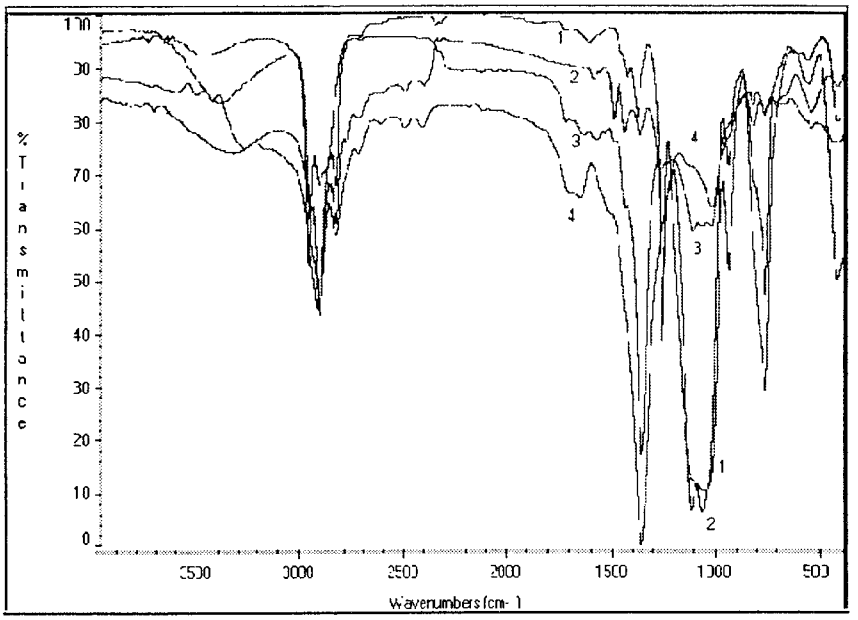

Figure 4: FTIR spectra of W 280 after hardening in an aluminium cup (1) and of the W 280 extract from treated bricks after 2 (2), 19 (3) and 27 (4) weeks of conditioning (20 °C, 40 % RH).

ville, this was also obtained when a catalyst was added. This phenomenon could not be explained for the moment.

Brick and limestone showed an increasing chemical reactivity between the reactive groups and the surface of the material at increasing temperature of conditioning. For exposure temperatures between 20 and 60 °C, the highest chemical reactivity of MU1469 is obtained for Gobertange, the lowest for Euville. In presence of a catalyst, the highest reactivity of MU1469 with the substrate is obtained for Gobertange and brick. However the former shows a higher weight loss during conditioning probably due to degradation reactions. In practice, this would indicate that the water repellent is performing better on brick than on Gobertange. Similar as without catalyst, the model compound could be extracted almost completely from the Euville. This phenomenom might reflect what is obtained in practice where the water repellents applied on Euville show lower effectiveness.

The results obtained for Massangis are between those obtained for the Gobertange and Euville.

Extractions of bricks treated with Wacker 280 and Goldschmidt Tegosivin HL100 have shown that the possibility to obtain a representative extract depends on the type of product used. The higher the fraction of tri- and tetra-functionalised compounds, the higher the crosslinking degree and the lower the possibility to obtain an extract representative for the original product.

Acknowledgement.

The authors thank the company Goldschmidt for kindly supplying MU1469.

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