

Sulphate Emissions from Automobile Exhaust

THE INFLUENCE OF A CATALYTIC EMISSION CONTROL SYSTEM

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The installation of platinum group metal catalysts on 1975 model year U.S. automobiles for control of CO/HC emissions has led to concern over the tendency of such catalysts to oxidise SO₂ to sulphuric acid aerosol. Examination of sulphate emissions from Johnson Matthey and Volkswagen test vehicles suggests that although there is some tendency to form sulphate, especially under highly oxidising conditions, the levels of sulphate are in general low. Comparison of measured sulphate conversion with thermodynamic equilibrium values shows that only a small fraction of the available exhaust SO₂ is converted to sulphate, and that the catalyst's ability to convert is short-lived. Future moves toward a three-way catalyst capable of simultaneously converting CO/HC and NO_x pollutants should eradicate any tendency towards sulphuric acid formation in automobile exhaust.

During the early part of 1975 considerable concern was expressed in the United States over the possibility of automobiles equipped with platinum group metal catalytic emission control systems producing large quantities of sulphuric acid aerosol. The fear that airborne

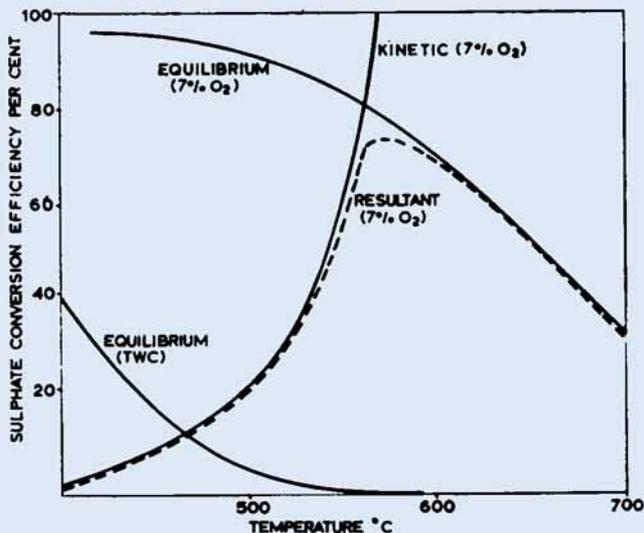
sulphate would rise to significant levels and endanger public health, as the catalytic emission controlled automobile population grew, largely contributed to the U.S. Environmental Protection Agency's decision to delay imposition of stricter carbon monoxide (CO) and hydrocarbon (HC) emission standards in February 1975. Since that time a great deal of information has been accumulated by workers in the field, aimed at (a) establishing a reliable sulphate emission test procedure in view of pending sulphate emission standards, (b) defining the influence of the emission control system on sulphate emissions, and (c) catalyst redesign to minimise sulphate emissions.

This article describes work carried out both at the Johnson Matthey Research Centre and in conjunction with Volkswagenwerk AG in order to assess the level of sulphate emission from cars equipped with Johnson Matthey automobile emission control catalysts.

Sulphate Formation in Automobile Exhaust

Sulphur compounds inherent in all petroleum based fuels are readily oxidised in the combustion chamber of an internal combustion engine to form sulphur dioxide (SO₂). It is now recognised that catalyst equipped cars can convert some sulphur dioxide to sulphur trioxide and hence to sulphuric acid. It is, of course, well known

Fig. 1 Sulphate emissions as a function of temperature for the concepts: oxidation catalyst + air pump (7 per cent O₂) showing equilibrium conversion efficiency curve and corresponding kinetic curve; and TWC, showing only the equilibrium conversion efficiency curve



that the catalytic oxidation of SO₂ to SO₃ followed by hydrolysis is the essential step in the manufacture of sulphuric acid, and that early processes used platinum to catalyse the oxidation reaction. Indeed the first kinetic study of this reaction was reported by Bodenstein and Fink in 1907 (1).

The oxidation of SO₂:



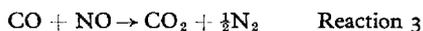
is an exothermic reaction and is controlled by thermodynamic limitations at temperatures above 450°C. Reaction (1) shows that the equilibrium concentration of SO₃ in the exhaust is proportional to the square root of oxygen concentration, and this fact has important consequences in the selection of an emission control system capable of minimising sulphate emission. Most 1975 model year vehicles have been equipped with a platinum group metal oxidation catalyst and an air pump for control of CO/HC emissions. The delivery of secondary air into the exhaust system prior to the catalyst results in high oxygen partial pressure causing the equilibrium in Reaction (1) to move to the right.

As a result of this, increasing emphasis is

being placed on catalytic emission control systems which minimise the amount of excess oxygen either by minimising the amount of secondary air addition, or by deleting the use of an air pump completely. The latter process calls for improved control of the air/fuel mixture entering the combustion chamber to ensure sufficient oxygen available at the catalyst for combustion of residual CO and HC during all driving modes. This approach has been employed by Volkswagen on the VW Beetle for the 1975 model year, using electronic fuel injection (EFI). In this case the engine is tuned lean to provide just sufficient oxygen for CO/HC combustion, but low O₂ partial pressures employed limit the equilibrium concentration of SO₃.

Advanced catalytic emission control systems incorporating NO_x control, take the electronic fuel injection concept a stage further with the development of "closed loop" EFI. This system employs an oxygen sensor in the exhaust system which maintains the air/fuel mixture at the stoichiometric value during all driving modes. Under such conditions it is possible to simultaneously catalyse the conversion of CO, NO, and HC pollutants using a "three way catalyst"

(TWC) according to the following reactions (simplified):

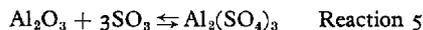


In this case the oxygen available for conversion of SO_2 to SO_3 is theoretically zero. In practice the excess oxygen in the exhaust is maintained at very low concentration, and hence sulphate formation is restricted to very low levels.

The above arguments regarding design of the emission control system are based solely on the effect of oxygen concentration on the thermodynamic equilibrium concentration of SO_3 formed over the catalyst, and therefore assume that the catalyst is sufficiently active to promote formation of SO_3 to the equilibrium values. Under such conditions a platinum group metal exhaust catalyst active enough to promote Reaction (1) to equilibrium, operating on an air pump equipped car burning fuel containing 0.03 weight per cent sulphur at 20 mpg could produce up to 150 mg/mile sulphate emission. In practice sulphate emissions from catalyst equipped cars rarely reach such high levels for the following reasons. Measured sulphate conversion levels on catalyst equipped cars have shown that the catalyst is usually insufficiently active below about 550°C to promote conversion of SO_2 to equilibrium levels. Above this temperature thermodynamic equilibrium limitations reduce the amount of sulphate formed. Figure 1 demonstrates this effect schematically by comparing the equilibrium and kinetic conversion levels over the typical operating temperature range of a catalyst equipped car. Two equilibrium conversion levels are shown, based on a high exhaust oxygen content (7 per cent) typical of an air pump equipped car, and a low exhaust oxygen content typical of closed loop EFI and TWC operation. Sulphate emissions will be the resultant of the equilibrium curves and the kinetic curve defining the catalytic reaction rate. Thus Figure 1 clearly demon-

strates that the TWC concept is preferable to the CO/HC catalyst plus air pump concept as a means of controlling sulphate emissions.

A second factor which can also contribute towards lowering sulphate emissions below equilibrium levels is the phenomenon of storage (2, 3, 4). This is generally attributed to the reversible interaction of SO_3 with the alumina support of the emission control catalyst according to Reaction 5.



This phenomenon is also capable of creating extremely high sulphate emission levels when stored sulphate is suddenly desorbed during high temperature excursions.

Sulphate Emission Measurement on Test Vehicles

Particulate sulphate, including H_2SO_4 aerosol, present in automobile exhaust is generally collected using the dilution tunnel technique. Filtered laboratory air is passed into a flow development tunnel, and the car's exhaust is admixed countercurrent with the air stream. An axial probe is inserted into the tunnel, and exhaust samples withdrawn isokinetically from the centre of the fully developed turbulent flow region. The samples are filtered, and the filter pads analysed for soluble sulphate.

All tests reported in this article were carried out either using the U.S. Federal Test Procedure driving cycle, or operating the car under steady state conditions.

The tests reported cover a range of emission control concepts. Thus Johnson Matthey test vehicles include a Chrysler Avenger, Leyland Marina, and Ford Capri equipped with CO/HC oxidation catalysts and air pumps. Catalysts were installed under floor in these cars, and a typical installation is shown on the Ford Capri in Figure 2. Sulphate emissions from these vehicles were measured at the Johnson Matthey Laboratories, and also at Ricardo Engineering, Shoreham-by-Sea. Sulphate emissions were also measured from two Volkswagen Beetles

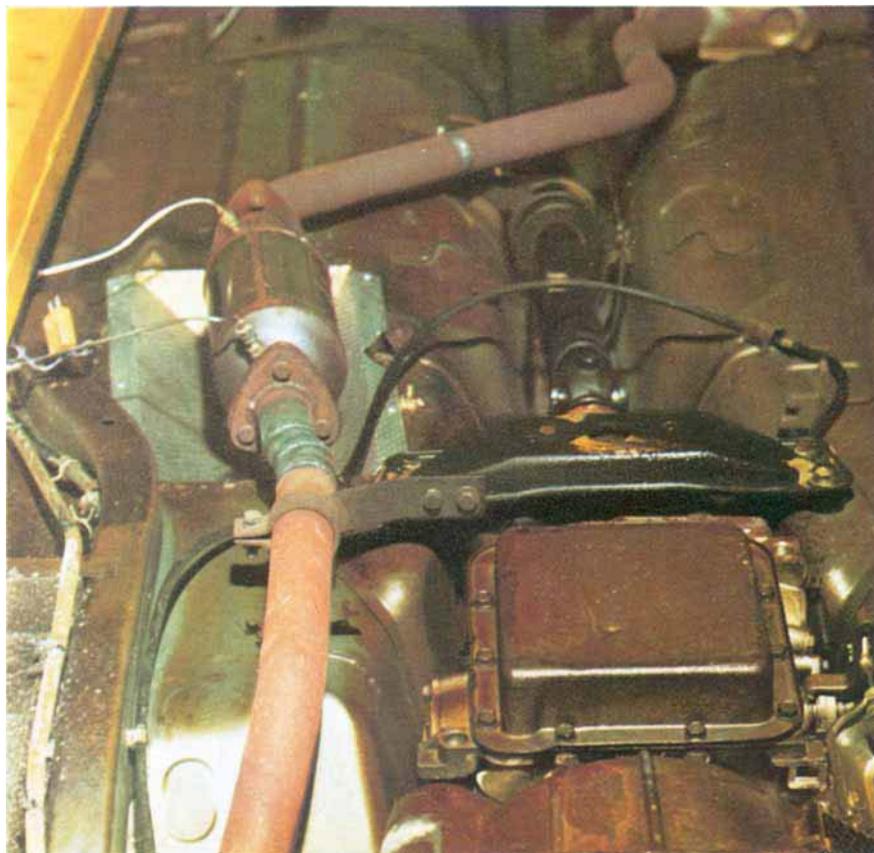


Fig. 2 Installation of an oxidation catalyst converter for control of CO and hydrocarbon emissions in the exhaust system of a 2 litre Ford Capri. The vehicle is provided with an air pump to supply secondary air to the exhaust to ensure excellent combustion of CO and HC pollutants over the catalyst

equipped with EFI and an oxidation catalyst. Secondary air was not used on these test vehicles, which were tested in a collaborative Johnson Matthey-Volkswagen programme conducted at Olson Laboratories, California. In addition, sulphate levels have been measured on a VW Beetle equipped with closed-loop fuel injection, oxygen sensor and Johnson Matthey three way catalysts. This test vehicle was kindly loaned to Johnson Matthey by Volkswagen for evaluation of three way catalyst systems. The three way catalyst installation on the VW Beetle is shown in Figure 3.

Concept 1: CO/HC Catalyst Plus Air Pump

The effect of secondary air on sulphate

emissions from a catalyst equipped Chrysler Avenger is shown in Table I.

Table I			
Sulphate Emissions over the FTP on EW2/3C/4 Oxidation Catalyst as a Function of Oxygen Concentration in the Exhaust			
Oxygen concentration in the exhaust was varied by changing the engine speed/air pump speed ratio.			
Exhaust oxygen per cent			Sulphate mg/mile
Max.	Min.	Average	
0.4	0.05	0.15	negligible
5.25	3.4	4.2	5.5
8.1	4.5	6.1	7.7
10	2.7	7.5	10.7

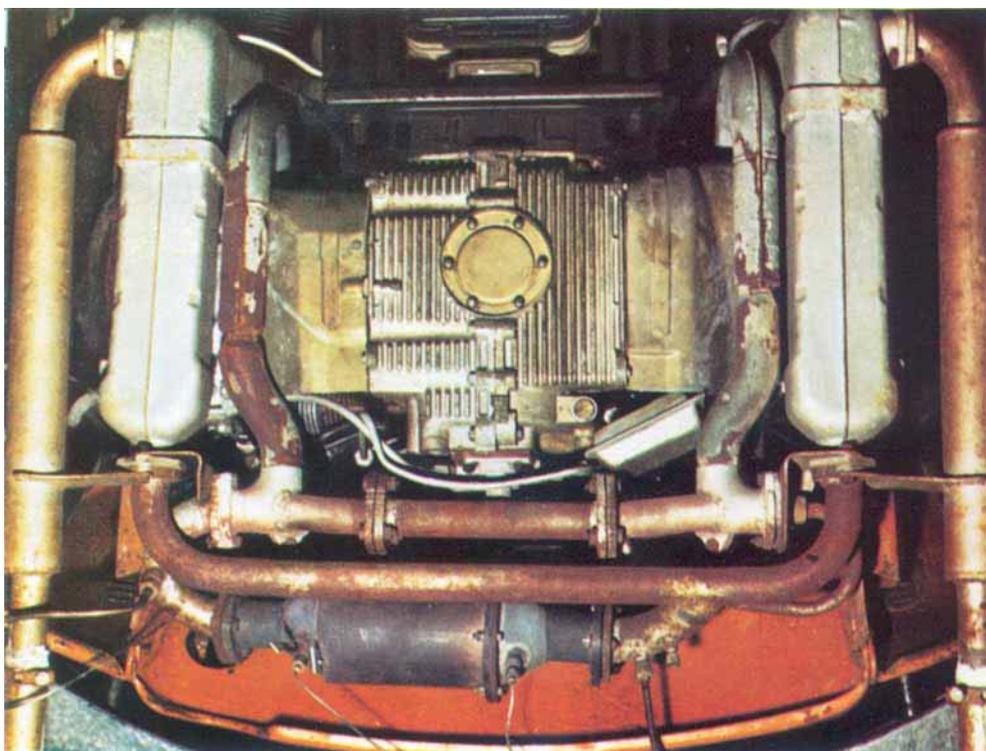


Fig. 3 Installation of an advanced Three Way Catalyst converter for control of CO, hydrocarbon, and nitrogen oxide emissions in the exhaust system of a 1.6 litre Volkswagen Beetle. The vehicle is fitted with a closed loop electronic fuel injection device provided with an oxygen sensor monitoring the exhaust upstream of the catalyst. In this way the air/fuel mixture is held at stoichiometric over all driving modes

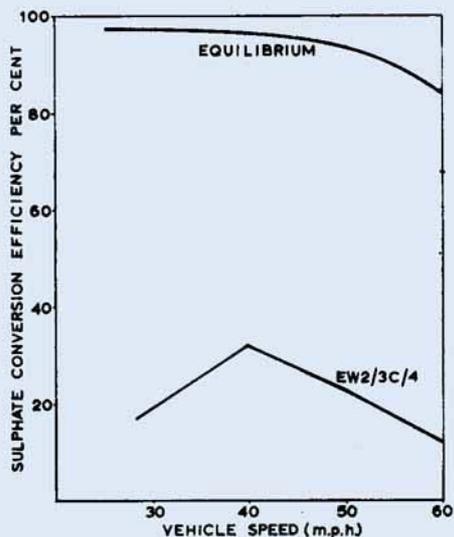
In this test the car was driven over the Federal Test Procedure, with the air pump operating at differing speeds. The increase in sulphate emissions with increasing exhaust oxygen content is in accord with both thermodynamic prediction, and published kinetic data for SO_3 formation over platinum catalysts (5).

In another test a Leyland Marina was driven under steady state conditions for 500 miles, and the maximum sulphate emission compared with predicted thermodynamic equilibrium values in terms of conversion of fuel sulphur to sulphuric acid. Tests using fresh catalyst for each steady state condition showed that although a steady increase in the vehicles sulphate emission occurred during early mileage accumulation, due to storage on the fresh catalyst surface, a well-defined maximum sulphate emission could be estab-

lished within 500 miles. Comparison of sulphate emissions with equilibrium levels predicted for each of the steady state conditions (Figure 4) shows that in tests up to 60 mph the maximum sulphate levels were substantially less than the equilibrium values. Maximum sulphate emissions in these tests were around 20 mg/mile, as compared to around 150 mg/mile predicted for equilibrium conversion. These data show that in such steady state tests the rate of catalytic oxidation controls the sulphate level in the exhaust and that the catalytic oxidation process is not sufficiently fast to reach the sulphate levels predicted from thermodynamic data.

The fact that the catalyst's surface reaction kinetics control the amount of sulphuric acid formed in the exhaust implies that the typical ageing processes experienced by the catalyst during mileage accumulation, such as sinter-

Fig. 4 Steady state sulphate conversion efficiency over EW2/3C/4 oxidation catalyst (with air pump). Comparison is made with the conversion expected if the catalyst was operating at equilibrium



ing and poisoning, should diminish the level of sulphate as the catalyst ages. Sulphate emissions obtained on several Johnson Matthey test vehicles with catalysts of varying mileage accumulation have been compiled (Figure 5). Data produced on Avenger, Marina, and Capri test vehicles using catalysts aged by different methods give an insight into the sulphate emission profile over a 50,000 mile test. During early mileage the sulphate levels climb rapidly as the storage capacity of the catalyst becomes saturated. After 200 miles the catalyst

apparently starts to deactivate until after about 10,000 miles the sulphate levels are similar to a non-catalyst equipped car (1 to 2 mg/mile). The loss of sulphate activity occurs at no loss to the catalyst's ability to meet CO and HC emission standards, as shown by the 50,000 mile data generated on the Ford Capri, where the same catalyst met statutory CO and HC standards (Table II).

A similar sulphate emission profile against mileage has been observed in the Volkswagen Laboratories. Tests on a VW Dasher equipped with an oxidation catalyst and an air pump,

Fig. 5 Sulphate emissions as a function of catalyst ageing. Both steady state and FTP ageing show a maximum in catalyst sulphate activity after only several hundred miles, followed by a steady decline in emissions

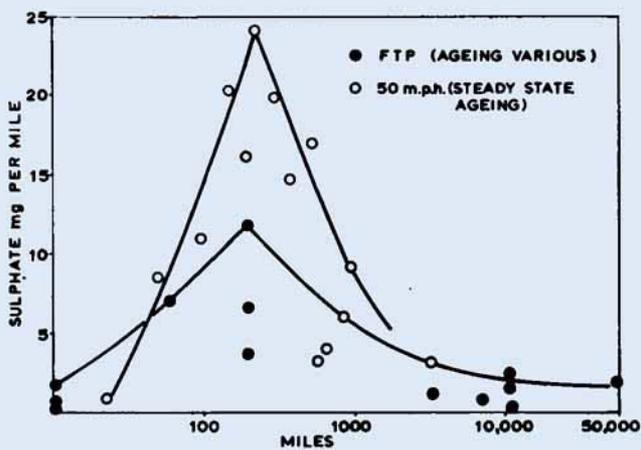


Table II CO/HC and Sulphate Emissions Obtained using a Ford Capri equipped with Johnson Matthey Oxidation Catalyst These data were obtained after the car had completed 50,000 road miles.			
	CO g/mile	HC g/mile	SO ₄ ⁼ mg/mile
Without catalyst	14.0	1.0	2.1
With 50,000 mile catalyst	2.2	0.23	1.9

and a VW Beetle equipped with an oxidation catalyst and EFI show (Table III) a decrease in sulphate emission during the high mileage portion of the durability test.

The trend in sulphate emission with mileage is not marked with the Dasher and is in all cases close to the vehicles SO₄⁼ emission without catalyst. Some increase is shown with the Beetle at around 5,000 miles, but the emissions never reach the 20 mg/mile levels observed in the Johnson Matthey tests using similar catalysts. This may reflect the fact that maximum sulphate levels are found around the 200 mile region of ageing (Figure 5) and the VW cars were not tested at this point. However, the fact remains that for the majority of the catalyst's life the sulphate

emissions are extremely low, and only reach appreciable levels during a relatively short period.

Concept 2: CO/HC catalyst, EFI, No Air Pump

Tests at Olsen Laboratories in the joint JM/VW programme examined the sulphate emissions of a new and 5,000 mile VW Beetle equipped with electronic fuel injection and a Johnson Matthey catalyst. Each vehicle was preconditioned by driving 200 miles at 50 mph and then the emissions were measured over the Federal Test Procedure (FTP) and at 30, 40, and 55 mph (Table IV).

Highest sulphate emissions were found at the high speed condition, probably reflecting the increasing tendency of the car to run lean (excess oxygen) at higher engine speeds. The 55 mph results reflect clearly the increasing role of sulphate storage at higher catalyst temperatures.

Thus the new car's sulphate emissions progressively increase as sulphate storage diminishes in each subsequent test, whereas the 5,000 mile car shows a decreasing level of sulphate emission as previously stored sulphate is released. In no case did these vehicles reach the 20 mg/mile plus values of sulphate emission found with the air pump equipped cars.

Table III Sulphate Emissions from VW Test Vehicles during Mileage Accumulation (All emissions in g/mile.)								
Miles	VW Dasher				VW Beetle			
	CO	HC	NO _x	SO ₄ ⁼	CO	HC	NO _x	SO ₄ ⁼
Zero	4.41	0.44	1.45	0.003	5.54	0.42	0.67	0.001
5,000	4.52	0.63	1.38	0.003	7.82	0.43	1.32	0.008
10,000	6.28	0.59	1.97	0.003	6.10	0.68	1.26	0.006
15,000	6.96	0.71	1.35	0.003	5.51	0.59	1.15	0.003
22,500	5.50	0.72	1.59	0.002	6.29	0.62	1.50	0.003
Without catalyst	23.88	2.40	2.43	0.0015	10.68	1.52	1.64	0.002

Test	Sulphate emission mg/mile							
	New car				5,000 mile car			
	FTP	30 mph	40 mph	55 mph	FTP	30 mph	40 mph	55 mph
1	0.9	0.3	4.7	6.5	2.2	0.3	4.4	11.6
2	0.8	0.2	6.7	7.7	2.0	0.4	3.7	10.8
3	1.0	0.2	13.1	8.4	0.6	0.2	1.9	6.1
4	0.7	0.2	13.0	11.0	1.4	0.2	2.0	7.2
5	6.0	0.1	10.7	18.0	0.8	0.3	4.3	8.5

Concept 3: Closed Loop Fuel Injection, O₂ Sensor and TWC

As shown previously the low exhaust oxygen levels obtained with the TWC concept inherently produce a low sulphate emitting vehicle. Tests on twenty prototype TWCs, including rhodium promoted catalysts, using the Volkswagen Beetle equipped with closed loop fuel injection confirm the low sulphate emitting characteristics of this advanced emission control concept. These catalysts have shown sulphate emissions as low as 0 to 6 mg/mile when fresh and 0 to 0.4 mg/mile after ageing on a test bed for 100 hours. In most cases the sulphate emissions are negligible, or less than 1 mg/mile, and only in one instance exceed 5 mg/mile. In the cases where the higher sulphate emissions are recorded, ageing the catalyst again substantially reduces the sulphate emission level.

Conclusions

Tests using Johnson Matthey catalyst equipped vehicles have shown that conversion of sulphur dioxide in the exhaust to harmful sulphuric acid occurs to a much lower extent than would be predicted from thermodynamic equilibrium considerations. Maximum conversion occurs after about 200 miles driving, and thereafter the catalyst's ability to produce harmful sulphate progres-

sively decreases, without a substantial loss in its ability to convert other pollutants (CO/HC/NO_x) to harmless substances. This suggests that the contribution of sulphate emissions from catalyst equipped cars to the urban environment could be substantially less than previously estimated.

Examination of sulphate emissions from different emission control concepts shows that limiting the amount of excess oxygen in the exhaust diminishes the tendency toward sulphate formation. Thus the move towards the three way catalyst concept for simultaneous control of CO/HC/NO_x in 1978 should virtually totally eradicate any tendency of a catalyst-equipped car to produce sulphuric acid aerosol.

References

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