⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 181 168**
A1

⑫ # EUROPEAN PATENT APPLICATION

㉑ Application number: 85307939.0

㉒ Date of filing: 01.11.85

(51) Int. Cl.^{4}: C 25 D 11/08
C 25 D 11/18, B 21 D 26/02

㉚ Priority: 05.11.84 GB 8427981

(43) Date of publication of application:
14.05.86 Bulletin 86/20

(84) Designated Contracting States:
BE DE FR GB IT NL SE

(71) Applicant: BL TECHNOLOGY LIMITED
106 Oxford Road
Uxbridge Middlesex UB8 1EH(GB)

(71) Applicant: ALCAN INTERNATIONAL LIMITED
1188 Sherbrooke Street West
Montreal Quebec H3A 3G2(CA)

(72) Inventor: Maddison, Anthony
27 Adonis Close Perrycrofts
Tamworth Staffordshire B79 8TY(GB)

(72) Inventor: Sheasby, Peter Geoffrey
71 Courtington Lane Bloxham
Banbury Oxon OX15 4HS(GB)

(72) Inventor: Davies, Nigel Cleaton
8 Byron Road
Banbury Oxon OX16 9RJ(GB)

(74) Representative: Unwin, Stephen Geoffrey
ARG Patent Department Cowley Body Plant
Oxford OX4 5NL(GB)

(54) **A method of fabricating structures from aluminium sheet and structures comprising aluminium components.**

(57) An anodising process in an acidic electrolyte preferably comprising phosphoric or sulphuric acid produces an anodic oxide layer on an aluminium sheet in a period of 2 minutes or less and, with appropriate conditions, in less than 15 seconds. The anodised sheet is formed into components which are secured together by adhesive and by localised mechanical fastening means such as spot-welds. The resultant structure may be of sufficient strength and durability to be used as the structural, load bearing parts of a motor vehicle body.

Croydon Printing Company Ltd.

A METHOD OF FABRICATING STRUCTURES FROM ALUMINIUM SHEET AND STRUCTURES COMPRISING ALUMINIUM COMPONENTS

This invention relates to a method of fabricating structures from aluminium sheet and structures comprising aluminium components.

The term "aluminium" as used here and throughout the specification is intended to include aluminium alloys.

It is well known for aluminium structures to be fabricated by bonding components together after having pre-treated the surfaces of the components. One such pre-treatment is DC phosphoric acid anodising as used in the aircraft industry, particularly by Boeing (British Patent 1,555,940), and this form of pre-treatment is considered to be one of the best available for long-term durability in structural applications. This durability is thought to depend on the structure of the oxide layer produced by DC phosphoric acid anodising under the Boeing conditions described and many papers have been written on this subject (eg J D Venables et al, Appl. Surface Science 3, 1979, 88-98). However, the Boeing process requires an anodising time of 5-60 minutes in a phosphoric acid electrolyte at a temperature of 10-30°C. In practice an anodising time of 20-30 minutes is usually used, and clearly this is only suitable for batch treatment of components rather than as a continuous treatment for aluminium coil. Although oxide layer thicknesses are not reported in the patent examples, in practice a minimum thickness of 300-400 nm appears necessary to achieve the desired properties.

Oxide layers produced by the Boeing process have excellent properties as adhesive substrates, to the extent that they constitute a standard to which the rest of the industry aspires.

It has also been proposed for aluminium structures to be "weld-bonded", that is bonded with adhesive but also spot-welded.

According to a first aspect of this invention there is provided a method of fabricating structures from aluminium sheet which comprises the steps of subjecting the aluminium sheet to an anodising process in an acidic electrolyte for a period of 2 minutes or less to form an anodic oxide layer thereon; producing components of a desired shape from the aluminium sheet; and securing two components together by adhesive and by localised mechanical fastening means.

According to a second aspect of this invention there is provided a structure comprising aluminium components which are secured together by adhesive and by localised mechanical fastening means and in which the components have an anodic oxide layer formed thereon by being subjected to an anodising process in an acidic electrolyte for a period of 2 minutes or less.

Preferred features of this invention will be apparent from the subsidiary claims of the specification.

The invention enables structures to be fabricated from aluminium components which have undergone a rapid pre-treatment but which nevertheless gives rise to bonds of strength and durability comparable to those achieved using the Boeing process.

Preferred forms of the invention also have the advantage that the anodising process can be carried out on aluminium sheet in coil form and can thus be effected continuously. Preferred forms of the invention also have the advantage of being spot-weldable.

Factors affecting features of this invention and their influence on preferred forms of the invention will now be discussed merely by way of illustration.

Equipment for continuous anodising of aluminium strip is well known, and is described for example in "Automation in Anodising" by W E Cooke (Aluminium Association, Aluminium Finishing Symposium, Chicago, March 1973). Suitable equipment includes an elongated bath with inlet and outlet ports for electrolyte and with opposed end faces having seals if necessary through which the continuous aluminium strip passes, the arrangement being such that the electrolyte preferably flows countercurrent to the strip. Two or more electrodes are positioned adjacent or indeed surrounding the moving strip, the electrodes being spaced in the direction of travel of the strip. Current leakage through the electrolyte is low because the electrolyte has a much lower conductivity than the metal.

In a preferred form of the invention the aluminium sheet is in the form of a coil for the advantage of rapid anodising and for convenience of storage and transport. In order for the anodising process to be carried out continuously, the tail of one coil may be joined to the head of the next so that the sheet can be continuously passed through a bath of electrolyte. Existing aluminium treatment plants generally have a line speed of at least 50 m/min, and often of 150-250 m/min. Thus, in order to avoid the need for very long electrolyte baths, the anodising process should take place rapidly. A contact time of 15 seconds between the sheet and the electrolyte is the longest that is likely to be practicable on existing plant. Electrolyte contact times of 1 to 6 seconds, and preferably 2 to 3 seconds, are likely to be convenient, and times as short as 0.5 seconds are possible. The electrolyte contact time at any particular line speed may be regarded as a fixed feature of the plant, and one about which the other process variables are adjusted. On certain types of plant much slower lines can be used and hence longer anodising times.

During the anodising process a satisfactory balance must be achieved between anodic oxide formation on the aluminium sheet and dissolution of the oxide in the acidic electrolyte. Sufficient anodic oxide must be grown to give adequate structural strength to the oxide layer and to provide an adequate surface area to provide a good substrate for adhesive. Equally, dissolution of the anodic oxide layer takes place so that the surface area is effectively enlarged by attack of the pore wall structure. However, this attack must not be sufficient to cause breakdown and powdering of the oxide layer.

Anodic oxide formation is essentially controlled by the anodising current density used. Anodic oxide growth per unit time is substantially proportional to anodising current density. With the short contact times available, the current density needs to be high to achieve a sufficiently thick oxide layer. The current density is preferably at least 250 A/m^2.

It is convenient to relate current density with electrolyte contact time in order to achieve a desired oxide thickness. This may be expressed by saying that the total anodising input will usually be in the range $2x10^4$ to $12x10^4$, particularly $3x10^4$ to $6x10^4$, C/m^2.

Film attack is essentially controlled by the nature, concentration, and temperature of the electrolyte, with temperature being the most important factor. In considering the nature of this attack, it needs to be borne in mind that an anodic oxide film is created at the metal/oxide interface, ie at the inner surface of the oxide layer remote from the electrolyte. Chemical dissolution occurs at the outer surface of the oxide layer, and it is thus the oldest remaining oxide that is subject to attack.

The anodising electric current is preferably AC so that the aluminium sheet is alternately anodically polarised (during which time oxide growth predominates) and cathodically polarised (during which time chemical dissolution of the oxide predominates). Biased AC wave forms may be employed with advantage to achieve the desired balance between anodic growth of the oxide layer and chemical dissolution. The AC frequency may be greater or (more likely) less than the standard 50 c/s. Alternatively DC may be employed, either continuously or as a pulsed current to increase the extent of chemical dissolution (between the pulses) relative to growth of the oxide layer.

The voltage is determined by the value of current density at which one has chosen to operate. Hence it finds its own level according to the current density and temperature (it is quite markedly effected by temperature at constant current density). For example at the lower end of the temperature range, eg at 35°C, the voltage is about 40V for 600 amps/meter^2. The voltage is reduced as the temperature goes up.

The temperature of the electrolyte is preferably at least 25°C for short anodising times. If the electrolyte temperature is too low, then no significant chemical dissolution of the oxide takes place during the (limited) electrolyte contact time and the surface area thereof is not increased. If the electrolyte temperature is too high, then chemical dissolution may outpace oxide growth to the extent that all oxide is redissolved as fast as it is formed. The preferred temperature range depends on the acids used in the electrolyte. Generally, with an acid that readily attacks aluminium oxide a lower temperature is needed than with an acid that attacks the oxide less readily.

Electrolyte concentration has a much less marked effect on the rate of chemical dissolution of the oxide film than temperature. The dissolution rate increases with electrolyte concentration and a concentration of at least 5% by weight of acid is found preferable in order to achieve rapid anodising.

The oxide layer formed on the aluminium sheet by the anodising is preferably relatively thin compared to that produced in the Boeing process. If the components are to be spot-welded (described below in more detail) the thickness of the oxide layer is preferably kept to 500nm or less otherwise the resistance of the layer may be too great to enable satisfactory spot-welds to be easily formed. The thickness of the oxide layer is also preferably at least 15nm as below this level controlled chemical dissolution of the oxide is difficult to achieve.

The anodising process can be carried out in a number of different electolytes based on acids such as phosphoric acid and sulphuric acid or other acids in which porous aluminium oxide layers are formed, such as chromic acid or oxalic acid. The electrolyte may also comprise a mixture of such acids.

A preferred electrolyte comprises from 5 to 15% by weight of phosphoric acid. Phosphoric acid is capable of strongly attacking the anodic oxide layer so it is difficult to achieve a balance between oxide formation and oxide dissolution during the anodising process particularly when short anodising times are needed to be compatible with existing process lines. With an anodising time of 15 seconds or less, the current density used should preferably be at least 250 A/m^2 and may be as high as can be achieved with the equipment used, eg up to 3000 A/m^2. A preferred current density range is 300 to 1500 A/m^2.

As phosphoric acid attacks aluminium oxide so readily, it is difficult to achieve sufficient oxide growth at high temperatures. It has not proved possible to generate an anodic oxide layer under AC conditions in a phosphoric acid electrolyte at 90°C even with a current density of 1250 A/m^2. When AC anodising is employed, the optimum electrolyte temperature is likely to be in the range 30 to 70°C. With DC anodising, somewhat higher temperatures up to 80°C may be useful.

With the optimum conditions described, anodising times as short as 0.5 seconds may be achieved.

A further advantage of using a phosphoric acid electrolyte is that the anodic oxide layer formed incorporates significant amounts of phosphate. Phosphate is known to be a hydration inhibitor with oxide surfaces, and as deterioration of the pre-treated surface often occurs through hydration of the oxide, at least at its surface, the presence of a hydration inhibitor at this point is beneficial.

Because the oxide is readily attacked by the hot phosphoric acid electrolyte, rapid rinsing of the oxide layer surface is required after anodising, and this is readily achieved in a continuous coil process.

The result of the phosphoric acid anodising process is an aluminium sheet carrying a porous anodic oxide layer which contains phosphate ions, the pores of which are enlarged so that the effective surface area of the oxide layer is increased. The oxide layer is generally 15 to 200 nm thick. With an electrolyte contact time of no more than 15 seconds, it is difficult to produce an oxide layer more than 200 nm thick.

Another preferred electrolyte comprises 10 to 30% by weight of sulphuric acid. Sulphuric acid attacks aluminium oxide less readily than phosphoric acid so the electrolyte is generally more concentrated and at a higher temperature than that used with phosphoric acid in order to maintain a sufficient dissolution rate of the oxide. With a sulphuric acid electrolyte the anodising process is preferably effected at a temperature of at least 50°C. The optimum electrolyte temperature is in the range 70° to 95°C.

With a current density of at least 250 A/m^2 and an electrolyte contact time of between 0.5 and 15 seconds, the oxide layer formed generally has a thickness of 300 nm or less.

Conditions similar to those described in UK Patent Specification No. 1235661 which discloses a method of anodising aluminium sheet in a sulphuric acid electrolyte in preparation for the application of lacquer may also be suitable.

After the anodising process, press lubricant which is selected to be compatible with the anodising process used and the adhesive subsequently applied, for instance Houghtodraw 7002 (Trademark) made by Edgar Vaughan Limited, is applied onto the oxide layer. The aluminium sheet is then cut into discrete lengths or is recoiled for ease of storage. Alternatively, the aluminium sheet can be cut into discrete lengths before the press lubricant is applied. It is also possible to recoil the aluminium sheet after the anodising process for storage and to apply the press lubricant after it has been uncoiled again, the sheet being cut into discrete lengths either before or after the application of the press lubricant. The press lubricant is preferably applied by machine, eg by spraying or roller coating, to ensure that a uniform coating is formed. As little press lubricant as is necessary for satisfactory forming is used - usually less than 20 grammes/square metre, and preferably less than 5 grammes/square metre. A light oil or separating agent such as dioctyl sebacate as used prior to coiling aluminium strip, or lacquer as used in the canning industry, are not suitable as press lubricants.

In some forming operations no press lubricant is required. Some structure can also be produced without any forming operation.

Having produced discrete lengths of aluminium sheet carrying the oxide layer and press lubricant by any of the routes described above, these are then formed into components of desired shapes. In the case of components for a motor vehicle body, this may involve pressing the sheet between dies and the punching of any holes required. An epoxide adhesive, for instance that produced by Permabond Inc under the Trade Mark ESP105, is then applied to the components which are assembled together in a jig. The components are then secured together by localised mechanical fastening means, for instance spot-welds, while the adhesive is still fluid. The structure can thus be removed from the jig before the adhesive has cured. The adhesive is cured for 10-30 minutes at a temperature of 150° to 180° or such other times and temperatures as are suitable for the particular adhesive used. Phenolic or acrylic adhesives can be used in place of the epoxide adhesive.

The anodised aluminium coil or cut sheets can be stored for up to 6 months in many typical storage conditions without any significant deterioration in the oxide layer. The oxide layer is thus capable of providing a sound base for a strong and durable adhesive bond even if the sheet is stored for a considerable time between the anodising process and the application of adhesive. In practice, it is essential that the anodised sheet is storage stable as there is often a delay of at least 48 hours (2 days) and usually more than 168 hours (7 days) between the anodising of the aluminium sheet at one site, eg at an aluminium mill, and the forming of the aluminium sheet into components of desired shape at another site, eg in a vehicle production line. The storage stability of the anodised aluminium sheet is, of course, enhanced if the press lubricant is applied before storage.

The aluminium sheet may be degreased before the anodising process but one advantage of AC anodising is that it renders the surface of the sheet cyclically anodic and cathodic with evolution of hydrogen at the surface. This tends to separate any grease or other contamination from the surface of the sheet so the contamination is lifted off the surface. Air agitation can also be used to assist in the removal of contamination. As mentioned above, the electrolyte may also be passed through the bath in a direction opposite to that of advance of the aluminium sheet so that any contamination in the bath is swept away from the area of the bath where the sheet emerges from the electrolyte.

The press lubricant applied to the oxide layer may be oil, grease or water based. The removal of an appropriately selected press lubricant remaining on the formed components prior to application of the adhesive is not necessary. Indeed, the complete removal of lubricant prior to application of the adhesive would be impracticable in a mass production line. The press lubricant may be pushed aside by the subsequently applied adhesive but may also become dispersed within the adhesive. The press lubricant should therefore be compatible with the anodised aluminium and with the adhesive so that it does not unduly affect bond durability and strength. The press lubricant should also be capable of ready removal prior to any painting operation even after being subjected to any elevated temperature at which adhesive has been cured.

The adhesive used in the joints should be capable of retaining its strength under a wide variety of conditions such as temperature and humidity. The adhesive should wet the surface it is applied to but preferably be such that it does not sag or drip when applied to a vertical surface. Thixotropic materials may thus be preferred. The adhesive may be applied by any suitable method and may be applied to form a layer from about 0.1 to 3.0 mm thick in the final joint depending on joint geometry. The adhesive is preferably sufficiently fluid to be squeezed out of the way at locations in the joint where pressure is applied by a spot-welding tool. It is also possible to use adhesive in a powdered or tape form. The adhesive is not usually applied over the entire surface of the components although this may be convenient when a powdered adhesive is used.

Resistance spot-welding is carried out through the adhesive whilst this is still in paste form using 5 mm truncated cone electrodes. An electrode pressure of 500 pounds (2.2 KN) is held for a time equal to 10 cycles of the electrical welding power prior to a 3 cycle weld at 23,000 amps, and is followed by a holding time of 10 cycles to allow the molten slug of aluminium produced to solidify. Adjacent welds are spaced about 6 inches to 1 foot (15 to 30 cms) apart.

It has been found that a structure formed in the manner described above is strong enough to be load bearing and has durable bonds which substantially retain their strength with time. It will be appreciated that besides holding the structure together when it is removed from the jig, the spot-welds or other localised mechanical fasteners also increase the strength of the joint between the bonded components and in particular increase the peel strength of the joint.

Although it is possible for the spot-welds to be carried out at locations where there is no adhesive, it will generally be found desirable to spot-weld at a position where there is adhesive, the spot-welding being carried out throught the adhesive before it has set.

As an alternative to spot-welding, the components may be rivetted together preferably using rivets which do not pierce both of the components so that the seal between the components is not broken. Other forms of localised mechanical fasteners such as those which involve localised mechanical distortion of the components to secure them together, eg Tog-L-Lok (Trade Mark) of the BTM Corporation, may also be used.

The aluminium sheet may be an aluminium alloy such as the 2000, 3000, 5000 or 6000 series of the Aluminium Association Incorporated Register. The optimum anodising conditions will generally differ for each alloy and tighter control of the conditions may be required with the 2000 Series than with the others to ensure that a satisfactory oxide layer is produced. It should also be noted that magnesium rich alloys of the 5000 Series form an oxide layer containing magnesium oxide (MgO) which is more soluble in acidic electrolytes so a lower temperature may need to be used with such alloys.

Examples of conditions used in the anodising process will now be given merely by way of illustration.

EXAMPLE 1

Panels of 5251 alloy were AC anodised in a 10% by weight phosphoric acid electrolyte at a temperature of 45°C and a current density of 600 A/m^2 for a period of 10 seconds. The panels were rinsed immediately after the anodising process. The panels were then bonded in a perforated lap-shear joint configuration using a toughened epoxy adhesive ESP105 (Trade Mark) produced by Permabond Inc. The initial bond strength was measured and the perforated joints were exposed to a neutral salt spray at 43°C for periods of 2, 4, and 8 weeks. At these intervals, samples were taken and the retention of initial bond strength monitored. As a control, material prepared as in British Patent specification 1555940 was also bonded and tested. This was 5251 alloy, DC anodised at 12V in 10% by weight phosphoric acid solution for 30 minutes.

Initial bond strengths were identical; after the elapse of 8 weeks the retention of bond strngth of the material prepared as described in Example 1 was 71.9% as compared to 70.1% for the DC prepared material. This demonstrates the potential performance of surfaces prepared by anodising using extremely short pre-treatment times.

EXAMPLE 2

In the second example, aluminium sheet 5251 alloy is degreased using trichloroethylene vapour. The sheet is then subjected to alkaline cleaning using a 10% by volume aqueous solution of Oakite NST (Trade Mark) at 50°C. The sheet is immersed in this solution for a period of 5 minutes and then rinsed in running water for a period of 5 minutes. This treatment resulted in a water break free surface. The surface is then deoxidised using a solution comprising 25g/l of potassium dichromate, 50g/l of sulphuric acid with small additions of fluoride, ammonium, aluminium, calcium and phosphate ions. A suitable solution is Deoxodiser No 1 (Trade Mark) produced by ICI plc. The sheet is immersed in this deoxodising solution for a period of 3 minutes and then rinsed in running water for a period of 10 minutes. This removes the pre-existing air-formed oxide layer. Next, the sheet is subjected to an AC anodising process for a period of 1 minute in a 10% by weight aqueous solution of orthophosphoric acid at 20°C with a current density of 80 A/m^2. The sheet is finally rinsed in running water for a period of five minutes.

With an anodising time of 1 minute this Example is applicable to a relatively slow moving line.

EXAMPLE 3

Example 3 is similar to Example 2 but the sheet was subjected to an AC anodising process for a period of 10 seconds in a 10% by weight aqueous solution of sulphuric acid at 90°C with a current density of 1200 A/m^2.

In order to assess the durability of the adhesive bonds formed in Examples 2 and 3, test strips were pre-treated and then bonded together using Permabond ESP105. A first set (D) of test strips was subjected to an AC anodising pre-treatment in phosphoric acid as described in Example 2 for 1 minute and a second set (E) to a similar pre-treatment for 2 minutes. A third set (F) was subjected to an AC anodising pre-treatment in sulphuric acid as described in Example 3 for 10 seconds. A set (C) of control strips were also tested. The control strips were vapour degreased and alkaline cleaned as described in Example 2 and then deoxidised in a solution comprising sodium dichromate and sulphuric acid in accordance with the Boeing 5555 specification. This involved a DC anodising process in a 12% by weight orthophsphoric acid electrolyte at a temperature of 20 to 25°C and at 10 volts for a period of 20 minutes.

Test strips for each of the sets C, D, E, and F were bonded together by the adhesive ESP105 (Trade Mark) as described above. The lap shear strength of these un-perforated bonds was tested after the test strips had been exposed to salt spray at 43°C for 2, 4, 8, 14, 27 and 48 weeks. The results obtained are illustrated by the accompanying graph which shows the failure strength of the un-perforated joints with respect to time for each of the sets. The strength retention after 48 weeks is also shown in Table 1.

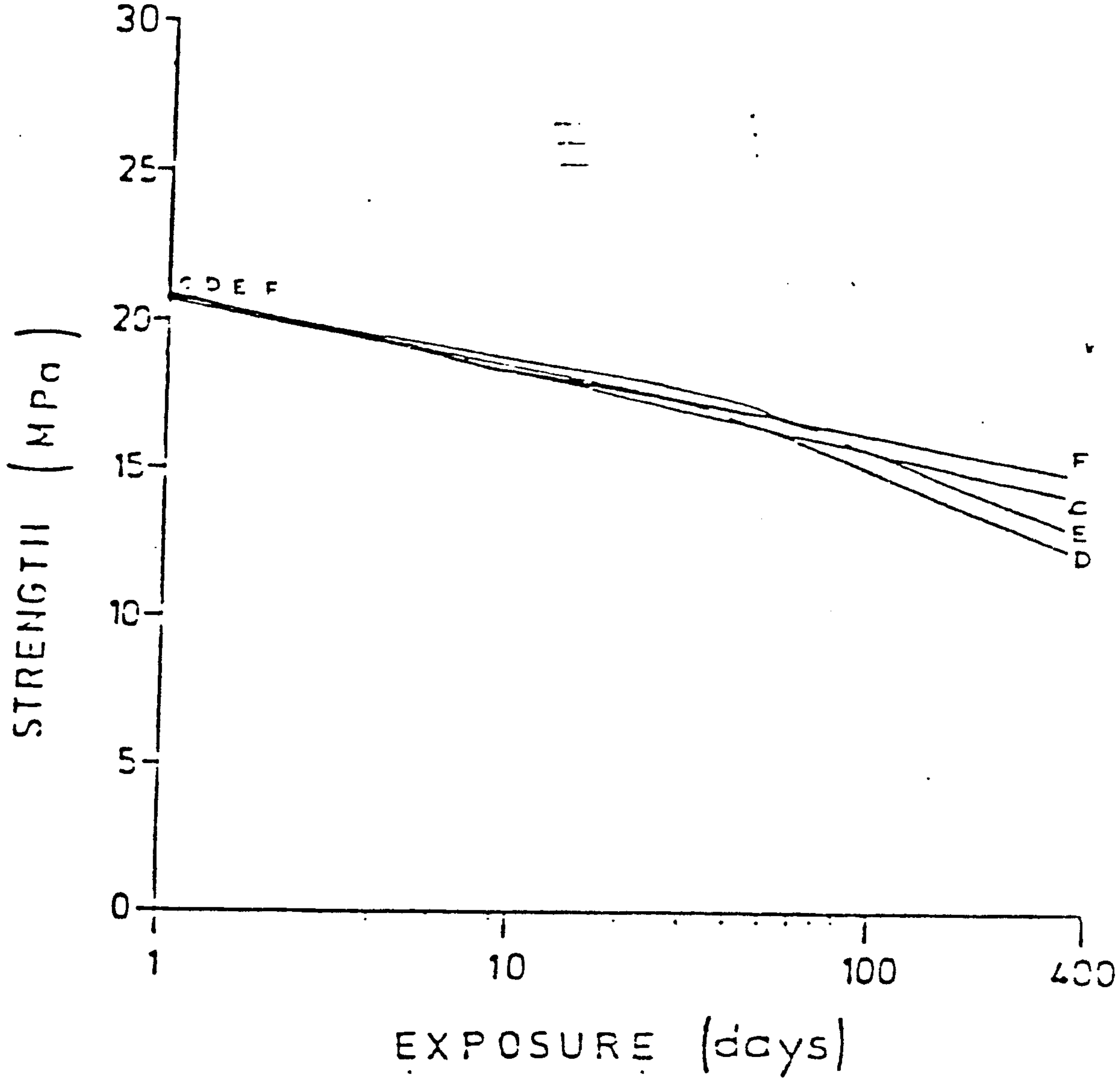
TABLE 1

PRE-TREATMENT	INITIAL FAILURE STRESS (MPa)	FAILURE STRESS AFTER 48 WEEKS (MPa)	STRENGTH RETENTION %
C	21.1 ± 0.3	14.6 ± 0.7	69.2
D	20.9 ± 0.4	12.5 ± 0.7	59.8
E	21.0 ± 0.6	13.2 ± 0.9	62.9
F	21.0 ± 0.5	15.2 ± 1.3	72.4

Strength Retention after 48 Weeks Exposure to Salt Spray

As will be seen, the strips pre-treated in sulphuric acid compare very favourably with those pre-treated by the BAC 5555 process. The strips pre-treated in phosphoric acid also show strength retention after 48 weeks only slightly lower than that achieved with the Boeing 5555 process. This should be contrasted to strips which have not been pre-treated at all and which would lose all strength within a few weeks. The great advantage of the AC anodising process as compared to the Boeing 5555 process is that it forms an oxide layer which gives good strength retention and which can be spot welded through. It would not be feasible to spot-weld through the oxide layer produced by the Boeing 5555 pre-treatment.

Graph



Comparison of durability of pretreatments C to F in salt-spray @ 45°C.

Example 4

In Example 4, aluminium sheet of 5251 alloy 0.7 to 2.0 mm thick is AC anodised in an electrolyte comprising 15% by weight sulphuric acid at a temperature of 80°C. The charge input at the surface of the sheet is arranged to be 12000 coulombs/M^2 which is achieved using a current density of 1200A/M^2 for a time of 10 seconds. This anodising process forms a porous oxide layer about 0.15 microns thick on the surface of the aluminium sheet.

In order to assess bond durability of joints formed on sheet anodised in this way and to make comparisons with other processes a number of tests were carried out.

In the first test, strips cut from 5251 aluminium sheet anodised in the manner described in Example 4 were bonded together and exposed to neutral salt spray for a range of times and the shear strength of the bonds then measured by the perforated lap shear method. Various thicknesses of oxide layer were used and the adhesive ESP105 mentioned above as well as that produced by the 3M Company under the Trade Mark EC2214 were used. Similar test strips were prepared from aluminium sheet which had undergone a conventional Boeing phosphoric acid anodising pre-treatment process (PAA) for 30 minutes and these were tested in the same manner for comparison. The results of these test are shown in Table 2. As will be seen, the AC anodising pre-treatment gives results similar to those using DC phosphoric acid anodising according to the Boeing process.

TABLE 2

SALT SPRAY TESTING

Pre-Treatment	Adhesive	Initial Bond Strength MN/m^2	Salt Spray Testing Time 2 Weeks		8 Weeks		20 Weeks	
			Bond Strength MN/m^2	% Strength Retention	Bond Strength MN/m^2	% Strength Retention	Bond Strength MN/m^2	% Strength Retention
PAA 30 min	2214	21.4	17.2	81.4	12.7	59.3	13.4	62.6
PAA 30 min	ESP 105	21.4	18.8	87.9	17.1	79.9	15.3	71.5
Hot AC 0.05 u) in sulphuric acid	2214	19.7	14.1	71.7	12.9	65.4	11.0	55.8
Hot AC 0.05 u)	ESP 105	21.3	18.9	88.6	17.2	80.6	15.2	71.3
Hot AC 0.15 u)	2214	21.2	17.1	80.6	13.4	63.0	12.7	60.1
Hot AC 0.15 u)	ESP 105	21.9	17.2	78.6	17.7	80.7	14.4	65.9
Hot AC 0.3 u)	2214	21.3	16.0	75.4	13.3	62.7	13.9	65.4
Hot AC 0.3 u)	ESP 105	20.8	18.8	90.7	16.3	78.6	14.4	69.6

Tests strips which had been pre-treated by the anodising process described above and then stored in various conditions before being bonded together were also tested. Three different storage conditions were used:

OD - Office Conditions (dry and relatively warm)
CW - Exposure in a deep shelter (cold and relatively humid)
HW - Humidity Cabinet (hot and relatively humid)

The results of these tests are shown in Table 3. Table 3 shows that the AC anodised pre-treated surface withstands storage in reasonable conditions for at least 6 months without affecting subsequent bond strength but rapidly deteriorates under hot wet conditions. This is similar to results found using conventional phosphoric acid anodising (not illustrated).

Finally, tests were carried out with bonded test strips being stressed and exposed to a humid atmosphere. These tests were also carried out on strips which had undergone pre-treatment by the Boeing phosphoric acid anodising process (PAA). The results of these tests are shown in Table 4. The results for strips with 0.05 microns thick oxide layer produced by AC anodising and those with a 0.15 and 0.3 microns thick layer are similar to those with the Boeing phosphoric acid anodising.

TABLE 3

EFFECT OF STORAGE BETWEEN PRE-TREATMENT AND BONDING

2214 Adhesive

Pre-treatment	Storage Conditions	Storage Time in Months	Bond Strength after Storage MN/m^2	Salt Spray Testing Time			
				2 Weeks	4 Weeks	8 Weeks	12 Weeks
				Bond Strength MN/m^2	Bond Strength MN/m^2	Bond Strength MN/m^2	Bond Strength MN/m^2
Hot AC (0.15 u) in sulphuric acid	OD	1	21.5	15.6	14.1	14.8	14.2
		2	21.4	15.7	14.6	14.7	14.3
		4	20.6	14.0	13.9	14.7	-
		6	22.3	15.7	14.6	15.3	14.9
(Initial Bond Strength 19.9)	CW	1	21.7	15.6	14.0	14.8	14.1
		2	21.1	15.0	13.5	14.2	14.0
		4	20.2	15.7	13.2	14.7	-
		6	21.7	15.4	14.5	14.9	14.9
2214 Adhesive	HW	1	7.8	4.9	3.8	4.6	4.3
		2	6.5	4.6	4.9	5.1	4.8
		4	8.2	4.3	2.8	4.1	-
		6	1.5	2.4	1.5	2.4	2.5

TABLE 4

HUMIDITY/STRESS TESTING (ADHESIVE ESP 105)

Pre-treatment		Initial Strength (MN/m^2)	Sustained Stress Level	Time to Failure (Days)		
				1st	2nd	3rd
PAA/30		20.1 ± 0.9	5	68	74	78
Hot AC 0.05u	in sulphuric acid	20.2 ± 1.8	5	78	96	135
Hot AC 0.15u		19.8 ± 2.1	5	52	63	78
Hot AC 0.3u		20.4 ± 1.5	5	55	67	68

Tests have also been carried out on strips which have been subjected to AC phosphoric anodising using a variety of conditions to determine whether they could be spot-welded through satisfactorily. An electrolyte comprising 10% by weight of phosphoric acid was used with a range of current densities. Each of the strips was anodised for a period of 2 mintues. The temperature of the electrolyte was 20°C but in the first test with a current density of $4000A/m^2$ the temperature rose to 40°C. This test was therefore repeated with the electrolyte maintained at a temperature of 10°C. It will be appreciated that as this test was conducted to test the weldability of anodised strips, the conditions used have been selected to maximise the thickness of the oxide layer formed and do not necessarily represent preferred conditions for producing strong durable joints. The conditions used and results achieved are summarized in Table 5. As will be seen, all the test strips could be satisfactorily spot-welded together.

A strip anodised in accordance with Example 3 was also tested and could be spot-welded satisfactorily.

The anodising process described above are believed to remove the air-formed oxide layer from the aluminium sheet and replace this by a new anodic oxide layer.

Table 5

Spot-Welding Strips Anodised in 10% by Weight Phosphoric Acid

Current Density (A/m^2)	Anodising Time (Minutes)	Temperature (°C)	Spot-welded? (Yes/No)
80	2	20	Yes
250	2	20	Yes
500	2	20	Yes
4000	2	20 → 40	Yes
4000	2	10	Yes

The new anodic oxide layer comprises a non-porous barrier layer portion and a porous structure above this barrier layer which together may have a total thickness of at least 30nm. Different conditions in the anodising process produce differences in the structure and proportions of these two components. The porous nature of the new oxide layer may provide a key to which the subsequently applied adhesive can be securely bonded. An increase in the surface area of the oxide layer thus tends to improve the bond which can be made to the subsequently applied adhesive. The porous structure formed by the anodic process is attacked by the acidic electrolyte so the initial pore structure is enlarged. This again increases the effective surface area of the oxide layer and permits better penetration of the subsequently applied adhesive into the pores. It has been found that structures formed in the manner described above can be strong enough to form the structural, load bearing parts of a motor vehicle body. Accelerated test also indicate tha such structures are capable of retaining adequate strength under the wide variety of conditions that a motor vehicle generally encounters for a time at least equal to the useful service life of the vehicle. The anodising processes described may be carried out much more quickly than many of the pre-treatments used in the prior art. The anodised sheet can be cut and formed without causing substantial damage to the porous oxide layer, even when the forming of the sheet involves pressing it between dies, so the oxide layer is still able to provide a base for strong and durable adhesive bonds. As the anodising process may also be effected before the sheet is cut into discrete lengths it can also be carried out continuously and can be carefully controlled.

CLAIMS

1. A method of fabricating structures from aluminium sheet which comprises the steps of: subjecting the aluminium sheet to an anodising process in an acidic electrolyte for a period of 2 minutes or less to form an anodic oxide layer thereon; producing components of a desired shape from the aluminium sheet; and securing two components together by adhesive and by localised mechanical fastening means.

2. A method as claimed in claim 1 in which the localised mechanical fastening means comprise spot-welds.

3. A method as claimed in claim 1 or 2 in which the anodising process is effected in an electrolyte comprising phosphoric acid, at a temperature in the range 25 to 80°C and with a current density of at least 250 A/m^2, and the aluminium sheet is subjected to the anodising process for a period of 15 seconds or less.

4. A method as claimed in claim 3 in which the anodising process is effected means of AC in an electrolyte comprising phosphoric acid in the range 5 to 15% by weight, at a temperature in the range 30 to 70°C and with a current density in the range 250 to 3000 A/m^2, and the aluminium sheet is subjected to the anodising process for a period in the range 0.5 to 15 seconds.

5. A method as claimed in claim 4 in which the anodising process is effected in an electrolyte comprising phosphoric acid in the range 10 to 15% by weight.

6. A method as claimed in claim 4 or 5 in which the anodising process is effected at a temperature in the range 50 to 60°C.

7. A method as claimed in claim 4, 5 or 6 in which the anodising process is effected with a current density in the range 600 to 3000 A/m^2.

8. A method as claimed in any of claims 4 to 7 in which the aluminium sheet is subjected to the anodising process for a period in the range 0.5 to 10 seconds.

9. A method as claimed in claim 1 or 2 in which the anodising process is effected in an electrolyte comprising at least 5% by weight sulphuric acid, at a temperature of at least 50°C and with a current density of at least 250 A/m^2.

10. A method as claimed in claim 9 in which the anodising process is effected by means of AC in an electrolyte comprising sulphuric acid in the range 10 to 30% by weight and at a temperature in the range 70 to 95°C, and the aluminium sheet is subjected to the anodising process for a period in the range 0.5 to 15 seconds.

11. A method as claimed in claim 10 in which the anodising process is effected with a current density of at least 1200 A/m^2.

12. A method as claimed in claim 10 or 11 in which the aluminium sheet is subjected to the anodising process for a period in the range 0.5 to 10 seconds.

13. A method as claimed in any preceding claim in which press lubricant is applied to the aluminium sheet after the anodising process and before the components are produced therefrom.

14. A method as claimed in claim 13 in which the aluminium sheet is initially coiled, is uncoiled before the anodising process and is re-coiled after the application of press lubricant.

15. A method as claimed in claim 14 in which the re-coiled aluminium sheet is uncoiled and cut into discrete lengths before the components are cut therefrom.

16. A method as claimed in claim 13 in which the aluminium sheet is initially coiled, is uncoiled before the anodising process and is cut into discrete lengths after the anodising process, the press lubricant being applied either before or after the aluminium sheet is cut.

17. A method as claimed in claim 16 in which the aluminium sheet is re-coiled after the anodising process and then uncoiled again before it is cut and before the application of press lubricant.

18. A method as claimed in claims 15, 16 or 17 in which the discrete lengths of aluminium sheets are formed in a press to produce the components.

19. A method as claimed in claim 18 in which the aluminium sheet, whether in coil form or in discrete lengths, is stored for at least 48 hours (2 days) after the application of press lubricant and before components are formed therefrom.

20. A method as claimed in claim 15 in which the aluminium sheet, whether in coil form or in discrete lengths, is stored for at least 168 hours (7 days) after the application of press lubricant and before components are formed therefrom.

21. A structure comprising aluminium components which are secured together by adhesive and by localised mechanical fastening means and in which the components have an anodic oxide layer formed thereon by being subjected to an anodising process in an acidic electrolyte for a period of 2 minutes or less.

22. A structure as claimed in claim 21 in which the localised mechanical fastening means comprise spot-welds.

23. A structure as claimed in claim 21 or 22 in which the anodic oxide layer has a thickness in the range 15-500 nm.

24. A structure as claimed in claim 23 in which the electrolyte comprises phosphoric acid and the anodic oxide layer has a thickness in the range 15-200 nm.

25. A structure as claimed in claim 23 in which the electrolyte comprises sulphuric acid and the anodic oxide layer has a thickness in the range 15-300 nm.

26. A structure as claimed in any of claims 21 to 25 in which the adhesive is an epoxide adhesive.

27. A structure as claimed in any of claims 21 to 26 which forms part of a motor vehicle body.

28. A structure as claimed in claim 27 which forms part of a structural, load bearing part of a motor vehicle body.

~~29. A method substantially as hereinbefore described with reference to the examples.~~

~~30. A structure substantially as hereinbefore described with reference to the examples.~~

European Patent Office

EUROPEAN SEARCH REPORT

0181168

Application number

EP 85 30 7939

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	TRANSACTIONS OF THE INSTITUTE OF METAL FINISHING, vol. 58, 1980, pages 81-84; P.J. THOMPSON et al.: "Pretreatment of aluminium by phosphoric acid anodizing prior to adhesive bonding" * Paragraph 3 *	1,2,5,16,21,22,26	C 25 D 11/08 C 25 D 11/18 B 21 D 26/02
A	RESEARCH DISCLOSURE, no. 132, April 1975, page 29;	3-8,12,21	
A	DE-A-2 507 386 (FUJI) * Example 2; claims *	5	
A	FR-A-2 382 330 (THE BOEING CO.)		
A	S. WERNICK et al.: "The surface treatment and finishing of aluminium and its alloys", vol. 1, 1972, pages 386-390, Robert Drager Ltd., Teddington, GB	9,13-18,23	
A	EP-A-0 001 198 (SCAL)		
A	FR-A-2 416 747 (SCHMALBACH)		

TECHNICAL FIELDS SEARCHED (Int. Cl.4)
C 25 D 11/04
C 25 D 11/06
C 25 D 11/08
B 21 D 22/20
B 21 D 26/02

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29-11-1985	VAN LEEUWEN R.H.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document
T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document