

1

3,592,680

METAL PLATING OF POLYOLEFINS

Raymond P. Bayer, Pierz, Minn., assignor to

Borg-Warner Corporation, Chicago, Ill.

No Drawing. Filed Aug. 29, 1968, Ser. No. 756,306

Int. Cl. B44d 1/092; C23c 3/02

U.S. Cl. 117—47A

10 Claims

ABSTRACT OF THE DISCLOSURE

A method of electrolessly plating a polyolefin substrate with copper, nickel or cobalt prior to application of an electrolytically deposited metal. A surface treatment step, which includes the application of an organophosphorus compound, is effective in promoting the adhesion between electroless metal layer and the polyolefinic substrate.

BACKGROUND AND SUMMARY OF THE INVENTION

This invention relates generally to the electroless deposition of metal onto a non-conductive substrate as a step preceding the electrolytic deposition of metal thereon. More particularly, the invention relates to a method of increasing the adhesion between the electroless metal layer and the substrate, which is particularly useful in the plating of aliphatic polyolefins.

While advances in the art of plating non-conductive substrates have been substantial in recent years, particularly with respect to the plating of acrylonitrile-butadiene-styrene graft polymers (ABS), the polyolefins have presented a number of problems. All such aliphatic polyolefins, such as polyethylene and polypropylene, exhibit a rather slippery or waxy surface texture because of (a) the essentially linear character of the olefinic polymer molecule, and/or (b) the low molecular weight exudate formed during crystallization. As a result, it has been found that the surface cannot be properly prepared by the use of conventional acid/chromate etchants.

In the present invention, it has been found that the use of various organophosphorus compounds as surface treating reagents can substantially increase the metal to substrate adhesion. Examples of such organophosphorus compounds are as follows: octyl diphenyl phosphite, triphenyl phosphite, tridecyl phosphite, phenyl didecyl phosphite, decyl diphenyl phosphite, decyl phenyl decanephosphonate, triphenyl phosphate, diphenyl methyl phosphate, tributoxyethyl phosphate, tri-iso-octyl phosphate, bis-nonylphenyl phenyl phosphate, trilauryl thio-phosphite, trinonyl phenyl phosphite, triethyl phosphite, diphenyl hydrogen phosphite, and tetra(nonylphenyl)poly(propyleneoxy) di-phosphite.

Whereas, conventional plating applications of polypropylene have yielded peel adhesion values of less than 1 lb. per inch, the use of the organophosphorus compounds are capable of consistently producing adhesion levels as high as 25 lbs. per inch.

The basic steps common to all known plating processes may be generally stated as follows: (1) preparation of surface by chemical etching or mechanical roughening, (2) catalytic sensitization with noble metal salts, e.g., PdCl₂, (3) electroless metal deposition, e.g., using a nickel-sodium hypophosphite bath, and (4) electrolytic deposi-

2

tion of metal. The principal factor affecting adhesion in this type of process is step (1) above; for if the surface is not properly prepared, the electroless metal layer will not cover the article in a uniform manner, and, therefore, will often result in misplate.

Accordingly, it is a principal object of the invention to provide an improved process for the electroless deposition of metal, such as, for example, nickel or cobalt onto a polyolefinic substrate.

Another object of the invention is to provide a novel surface pre-treatment for polyolefins which improves adhesion between the electrolessly deposited metal layer and the substrate.

Additional objects and advantages will be apparent from reading the following detailed description of the invention.

DETAILED DESCRIPTION OF THE INVENTION

For purpose of this disclosure, reference will be made to polyolefins which include the principal commercial polymers polyethylene and polypropylene, and, also, the more recently introduced commercial polyolefins such as poly-4-methylpentene-1, polybutene-1, and such copolymers as poly(ethylenepropylene), insofar as they can be formulated with the general properties of a thermoplastic. It is understood, however, that halogenated and other substituted polyolefin derivatives could also be employed. Also, while the main thrust of the invention is directed to a process which deposits an electroless nickel layer followed by electrolytically deposited metals such as nickel and chromium, it is not applicant's intention to limit the surface pre-treatment for use with a specific electroless-electrolytic plating process.

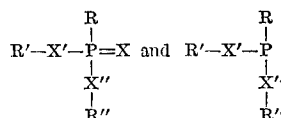
In order to illustrate the various examples by which the improved process has been successfully employed, it should be recognized that the surface treatment may be accomplished in several ways: (1) direct application of the reagent to the surface of a molded plastic article by dipping or spraying, and (2) dry blending the reagent with the resin prior to injection molding.

Some of these methods described above may be more useful in one application than another. The organophosphorus compounds are somewhat volatile, and may make it difficult to store the resin. Also, these compounds are rather hygroscopic, and absorption of water vapor reduces their effectiveness.

SURFACE TREATMENT

The surface treatment may be considered as two principal operations. In one embodiment of the process, a molded article to be plated is immersed into a bath containing essentially an organophosphorus compound of the type described above. It should be understood, however, that other techniques for applying the organophosphorus reagent to the surface, such as by spraying or melt blending, may also be used.

The class of organophosphorus compounds suitable for this application may be defined by the following generic structures:



wherein:

R is selected from the group alkyl, alkaryl, aralkyl, aryl, alkoxy, alkaryloxy, aralkoxy, aryloxy, alkoxyalkyl, alkylthio, alkarylthio, aralkylthio, arylthio, hydrogen, hydroxy and mercapto.

R' is selected from the group alkyl, alkaryl, aralkyl, aryl, alkoxyalkyl and hydrogen.

R'' is selected from the group alkyl, alkaryl, aralkyl, aryl, alkoxyalkyl, polyakyleneoxy and divalent hydrocarbyl (including alkylene, arylenes, alkarylenes and arylalkylene) attached to an oxygen or sulphur or another phosphate, phosphite or phosphonate radical.

X, X' and X'' are each selected from the group oxygen and sulphur.

Following the preliminary organophosphorus treatment, the part is rinsed in methanol, or another suitable solvent, to remove the residual surface conditioner. The article is then rinsed in water, treated with a mild alkaline cleaner, and rinsed again in water.

After thorough rinsing, the part to be plated is immersed into a bath containing a chemical etchant. These chemical etchants, many examples of which may be found in the published literature, preferably contain mixtures of concentrated mineral acids, for example, phosphoric and/or sulfuric, and may include chromium compounds. If the etchant does contain chromium, it is desirable to remove all traces of the etchant before proceeding to the electroless plating baths. Accordingly, the part is transferred to another solution commonly referred to in the art as a "chrome-kill" (or "chrome neutralizer"). This solution may comprise a dilute mineral acid, such as sulfuric acid, or mixtures of different mineral acids.

ELECTROLESS DEPOSITION

The electroless deposition process may be of several known types, such as, for example, those described in the specification of U.S. Pat. 3,011,920, issued to C. R. Shipley, Jr. on Dec. 5, 1961. In the conventional electroless plating process, metal deposition takes place in two stages: (1) sensitization of the substrate surface by means of a catalytic metal; and (2) deposition of the primary metal by means of a reducing agent.

In general, the surface of the substrate, after being properly etched by the process described above, is immersed into a bath containing the catalytic metal and thereafter, the catalyzed substrate is removed to a bath containing the deposition solution which ordinarily contains a salt of nickel, cobalt, copper, silver, gold, chromium or members of the platinum family, and a reducing agent, commonly formaldehyde, a hypophosphite salt, or dimethylamineborane.

The various combinations of catalyst and deposition metal are known in the art. For example, the following metals have been reported to be catalytic to the deposition of nickel and cobalt: copper, beryllium, aluminum, carbon, tungsten, tellurium, cobalt, platinum, silver, boron, thallium, vanadium, titanium, nickel, gold, germanium, silicon, molybdenum, selenium, iron, tin and palladium, with the precious metals gold, palladium and platinum being preferred. The same metals are catalytic to the deposition of copper, lead, platinum, rhodium, ruthenium, osmium, iridium, iron, silver, aluminum, gold, palladium, and magnesium, with gold, platinum, and palladium being preferred. Cobalt, nickel, and particularly iron have also been used to catalyze the deposition of chromium.

After removal from the electroless plating bath, the article is rinsed to remove residual electroless metal solution, and then electrolytically plated by any conventional method. One preferred series of electrolytically applied metals is (1) copper (to reduce the effect of thermal shock), (2) nickel, and (3) chromium. It should be understood, however, that any electrolytically deposited metal, or combination thereof, may be used in conjunction with this process.

The following examples are intended to illustrate various procedures for (1) testing adhesion values, (2) polypropylene plating by immersion in organophosphorus surface conditioner, (3) polypropylene plating by dry blending surface conditioner with resin pellets prior to molding, (4) plating of polyethylene by immersion in surface conditioner, and (5) plating of poly-(ethylene-butene) copolymer.

EXAMPLE I

Unless otherwise specified, all of the testing procedures involve the use of standard, injection molded plaques of a rectangular form measuring approximately 3" x 5" x 1/8". Adhesion values were tested by means of a procedure which is a variation of ASTM adhesion test D-429-64, Method B.

The apparatus used to test adhesion, commonly referred to as a tensometer, has a fixed cross head, a movable cross head, a device for continuously recording the applied load, and means for separating the cross heads at a constant rate, preferably about one inch per minute. A supporting jig attached to the fixed cross head supports the test specimen and insures that the load is applied at approximately 90° to the plastic surface throughout the test period.

Initially, the plated plaques are trimmed to fit the supporting jig, and then the metal layer is cut to form two parallel strips approximately one inch wide on the surface of the plaque. The metal layer is then peeled back manually so that approximately 1/2 inch is available for gripping by the movable cross head. Pieces of reinforcing tape with an adhesive surface are then applied to both sides of the 1/2 inch tab. In order to further insure comparable results, each of the specimens was pre-conditioned for at least four hours at the same temperature and humidity conditions (approximately 70° F.; 50% RH).

After the specimen has been placed in the tensometer, the test is begun by separating the jaws at approximately one inch per minute while the applied load is recorded continuously. This is carried out until the first metal strip is completely detached from the plastic substrate. The second strip is then tested in the same manner and the numerical values for adhesion are obtained by taking the mean of the maximum and minimum loads recorded on each of the two strips, adding them together, then dividing the sum of the means by two. These numerical results, expressed in pounds per inch (the width of the strip), are the average load required to separate a strip of metal plating one inch wide from the plastic substrate.

EXAMPLE II

Polypropylene plating by immersion

Samples of at least three commercially available polypropylene resins, i.e., (1) an injection molding polypropylene with a nominal melt flow of 5 gms./10 min.—ASTM D-1238-62T, (2) a general purpose flame retardant grade with a nominal melt flow of 5.0 gms./10 min., and (3) a general purpose homopolymer with a nominal melt flow of 4.0 gms./10 min. were molded into plaques as described in Example I.

The above-identified samples of polypropylene were used to examine the effect of various organophosphorus compounds, particularly octyl diphenyl phosphite, in the adhesion levels of a conventional electroless plating system. The general procedure may be outlined as follows:

- (1) Immersion in organophosphorus compound bath
- (2) Methanol wash at room temperature (or acetone as noted)
- (3) Water rinse
- (4) Cleaner (e.g., dilute alkaline cleaner) at 40-50° C. for 3 minutes
- (5) Water rinse
- (6) Chemical etch bath (Type A)
- (7) Water rinse
- (8) Chrome neutralizer (dilute mineral acid)

- (9) Water rinse
- (10) Catalyst
- (11) Water rinse
- (12) Accelerator (dilute mineral acid)
- (13) Water rinse
- (14) Electroless nickel bath
- (15) Conventional electroplating

Of the various organophosphorus compounds tested, the most effective is octyl diphenyl phosphite, although other such compounds give essentially equivalent results as discussed below. A number of factors influence the performance of octyl diphenyl phosphite: (1) Efficient stirring seems to be very essential for good coverage and adhesion. Since air tends to be absorbed on the surface of the plastic, reducing the effectiveness of the octyl diphenyl phosphite treatment, air agitation is not recommended. (2) Water has a detrimental effect on the performance of the organophosphorus compound at treatment temperature below 100° C. Provided the humidity is low, these baths may be cycled through 110° C. and used at temperatures between 90° and 100° C. with no adverse effects. (3) Recommended operating temperatures are between 100–110° C. Since adhesion values have been observed to be as high as 73 lbs./inch strip using pretreatment temperature of 90° C., some low adhesion values of 90° C. and 95° C. are probably the result of absorbed water. Octyl diphenyl phosphite has not been effective at operating temperature substantially below 90° C.

A large number of organophosphorus compounds were evaluated at 90° C. (Table I), and at 100° C. (Table II).

As used herein, the "catalyst" refers to the palladium-tin catalyst substantially as described in Example 2 of the aforementioned 3,011,920 patent; the "accelerator" is a dilute mineral acid; the electroless nickel solution is a bath, adapted to be operated at a temperature less than 100° F. with an alkaline pH, and containing about 4 to 10 oz. per gallon of nickel salts, 4 to 12 oz. of hypophosphite salts, and various conventional complexing and stabilizing compounds.

The chemical etch, Type A, is a solution containing (approximately) 70 gm. CrO₃; 1000 ml. H₂O; 1000 ml. phosphoric acid (85%) and 1600 ml. sulfuric acid (95.6–96.5%); the chemical etch (Type B) is a solution containing (in approximate parts by weight):

NaCr ₂ O ₇	102
Sulfuric acid (95.6–96.5%)	2930
Phosphoric acid 85%	1825
Water	1020

Referring now to Tables I and II, it can be seen that several of these compounds produced relatively high adhesion levels.

TABLE I

[Evaluation of various organophosphorus at 90° C. as pretreatment reagents for the plating of polypropylene using the recommended general plating procedure]

Immersion time (min.)	Adhesion (lbs./inch strip)			
	5	10	15	20
Compound:				
Octyl diphenyl phosphite.....	27.5	35+	33.8	31.4
Do	12.0	21.5	21.0	---
Decyl diphenyl phosphite.....	29.5	31.4+	31.0+	27.0
Do	14.8	11.3	16.1	17.3
Phenyl didecyl phosphite.....	37.5+	28.8	29.7	---
Bis (nonylphenyl) phenyl phosphite.....	0.4	0.4	0.4	0.4
Tetra(nonylphenyl) poly(propyleneoxy) diphosphite.....	0.5	0.4	0.5	0.4
Decyl phenyl decanephosphonate.....	0.2	0.2	0.4	0.3
Tri-iso-octyl phosphate.....	19.5	16.3	16.2	15.7
Tri(butoxyethyl) phosphate.....	---	7.1	8.6	7.7
Triphenyl phosphite.....	0.2	0.2	0.2	0.2
Do	0.1	0.1	0.1	0.1
Tridecyl phosphite.....	23.0+	27.0+	31.0+	---

TABLE II

[Evaluation of various organophosphorus compounds at 100° C. as pretreatment reagents for the plating of polypropylene using the recommended general plating procedure]

Immersion time (min.)	Adhesion lbs./inch strip				
	3	5	10	15	20
Compound:					
Octyl diphenyl phosphite.....	37.2+	---	---	---	---
Octyl diphenyl phosphite (Acetone wash).....	---	38.7	---	---	---
Octyl diphenyl phosphite.....	31.5	19.2	17.2	25.4	---
Triphenyl phosphite.....	23.7	11.8	12.8	10.5	---
Tridecyl phosphite.....	24.5	22.2	22.8	23.7	---
Phenyl didecyl phosphite.....	15.3	14.5	16.0	17.9	---
Decyl diphenyl phosphite.....	23.8	19.2	17.0	20.5	---
Decyl phenyl decanephosphonate.....	1.6	6.7	19.6	21.2	---
Triphenyl phosphate.....	0.2	2.2	0.2	0.2	---
Tri(butoxyethyl) phosphate.....	16.9	14.1	12.8	13.0	---
Tri-iso-octyl phosphate.....	14.4	6.4	6.1	7.0	---
Bis (nonylphenyl) phenyl phosphite (Acetone wash).....	1.4	1.6	2.2	2.1	---
Tetra(nonylphenyl) poly(propyleneoxy) diphosphite (Acetone wash).....	1.3	1.9	2.8	6.6	---
Trilauryl thiophosphite (Acetone wash).....	19.3	18.8	13.0	20.8	---
Tri(nonylphenyl) phosphite (Acetone wash).....	0.5	0.9	1.0	1.2	---
Trimethyl phosphite (95° C.).....	0.6	0.3	0.2	0.1	---
Diocetyl hydrogen phosphite.....	26.3	18.2	20.6	27.8	---
Triethyl phosphite.....	7.1	8.2	10.8	9.9	8.9
Tetraphenyl di(propyleneoxy) diphosphite.....	33.5	30.0	25.0	24.8	---

EXAMPLE III

Polypropylene plating by dry blending

General purpose polypropylene resin pellets (an injection molding grade polypropylene with a nominal melt flow of 5 gms./10 min.—ASTM D-1238-62T) were coated with octyl diphenyl phosphite in a conventional mixer-cooler (commonly referred to in the trade as a Henschel blender), molded into standard plaques and plated, all in accordance with the following procedure:

- (1) Pellets dried at 180° F. for 2 hours
- (2) warm pellets blended in Henschel with ODP for 10 minutes
- (3) standard plaques (Example I) were molded in a 5 oz. Stubbe reciprocating screw injection molding machine under the following conditions.
 - (a) melt temperature, 425° F.
 - (b) cylinder front, 420° F.
 - (c) cylinder center, 400° F.
 - (d) cylinder back, 350° F.
 - (e) nozzle rheostat, 100 volts
 - (f) mold cavity, 150° F.
 - (g) mold core, 150° F.
 - (h) ram pressure, 15,000 p.s.i.
 - (i) clamp pressure, max.
 - (j) overall cycle, 50 sec.
 - (k) clamp time, 30 sec.
 - (l) mold open time, 3 sec.
 - (m) screw speed, 75 r.p.m.
 - (n) back pressure, 1000 p.s.i.
 - (o) ram speed, 7 sec. (fill time)
- (4) Electroless nickel plating procedure was as follows:
 - (a) dilute alkaline cleaner at 45–50° C. for 5 minutes
 - (b) water wash
 - (c) Chemical Etch B at 70–75° C. for 5–30 minutes
 - (d) water wash
 - (e) catalyst at room temperature for 3 minutes
 - (f) water wash
 - (g) accelerator at room temperature for 3 minutes
 - (h) water wash
 - (i) Electroless Nickel bath at room temperature for 5 minutes
- (5) Conventional electroplating

7

The concentration of the octyl diphenyl phosphite (ODP) is important. With 2 weight percent ODP, no electroless plating could be effected. Three weight percent ODP will afford platable polypropylene, however, considerable misplate was observed and the plaques are easily under and overetched. Four weight percent ODP will afford a good plating grade polypropylene. The advantage of 5 weight percent ODP with the polypropylene is that a shorter etch time can be used to obtain the maximum adhesion of 40–50 lbs./inch strip (5–10 minutes), and over-etching is eliminated.

Molding conditions are of some importance to the adhesion. With respect to adhesion, plaques molded at a stock temperature of 450° F. and ram speed of 4 seconds and plated with an etchant time of 10 minutes afforded an adhesion value of 30.0 lbs./inch strip, while the plaques molded at a melt temperature of 425° F. and ram speed of 7 seconds and plated with an etchant time of 10 minutes afforded an adhesion value of 46.9 lbs./inch strip.

Some advantages of this method are: (1) no water problem, thereby affording better day-to-day adhesion results; (2) shorter etchant times; (3) elimination of bulk pre-treatment; and (4) elimination of organic rinses after bulk pre-treatment.

EXAMPLE IV

Polyethylene plating by immersion

Samples of high density polyethylene (a high density polyethylene ASTM Type III with a nominal melt flow of 5.0—ASTM D-1238-62T) were molded into the standard plaques described in Example I and processed in the following manner:

- (1) Immersion in octyl diphenyl phosphite 44–70° C. for 5–20 minutes
- (2) Methanol wash at room temperature (thorough)
- (3) Water rinse
- (4) Alkaline cleaner at 45–50° C. for 3 minutes
- (5) Water rinse
- (6) Chemical etch at 75° C. for 20 minutes (Type A)
- (7) Water rinse
- (8) Chrome Neutralizer at room temperature for ½ minute
- (9) Water rinse
- (10) Catalyst at room temperature for 2 minutes
- (11) Water rinse
- (12) Accelerator at room temperature for 3 minutes
- (13) Water rinse
- (14) Electroless Nickel at room temperature for 5 minutes
- (15) Water rinse
- (16) Conventional electroplating

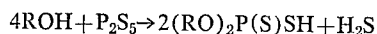
Adhesion values, measured in accordance with Example I, were found to be as high as 12.9 lbs./inch of strip when operating with 70° C. surface conditioner and about 8.1 lbs./inch of strip when operating at 44–53° C.

EXAMPLE V

A sample of butene-ethylene copolymer was molded into standard plaques (see Example I) and processed in the same manner as the polypropylene of Example II. Using an octyl diphenyl phosphite surface conditioner at 70° C., adhesion values of about 3.4 lbs./inch of strip were recorded.

EXAMPLE VI

Other organophosphorus compounds suitable for use in the present invention may be prepared by the following reaction:



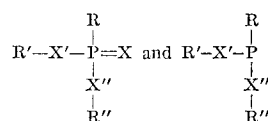
8

For example, a reaction mixture of one mole (130 g.) of 2-ethylhexanol, one quarter mole (55.6 g.) of phosphorus pentasulfide, 100 ml. xylene, and 100 ml. 85 vis. neutral oil is reacted for four hours with stirring over a steam bath. At the end of this time, the product is filtered yielding a mineral oil/xylene solution of 0,0' di-2-ethylhexyl phosphorodithioic acid.

While this invention has been described in connection with certain specific embodiments thereof, it is to be understood that this is by way of illustration and not by way of limitation; and the scope of the appended claims should be construed as broadly as the prior art will permit.

What is claimed is:

1. In the method of electroless deposition of a metal on an aliphatic polyolefinic substrate which includes the steps of chemically etching, sensitizing, and chemically reducing a salt of said metal onto the surface of said substrate, the improvement which comprises treating the surface of said substrate prior to chemically etching said surface with an organophosphorus compound of the group consisting of:



wherein:

R is selected from the group consisting of alkyl, alkaryl, aralkyl, aryl, alkoxy, alkaryloxy, aralkoxy, aryloxy, alkoxyalkyl, alkylthio, alkarylthio, aralkylthio, arylthio, hydrogen, hydroxy and mercapto.

R' is selected from the group consisting of alkyl, alkaryl, aralkyl, aryl, alkoxyalkyl and hydrogen.

R'' is selected from the group consisting of alkyl, alkaryl, aralkyl, aryl, alkoxyalkyl, polyalkylenoxy and divalent hydrocarbyl (including alkylene, arylene, alkarylene and arylalkylene) attached to an oxygen or sulphur or another phosphate, phosphite or phosphonate radical.

X, X' and X'' are each selected from the group consisting of oxygen and sulphur.

2. The method as defined in claim 1, wherein the article is immersed in said organophosphorus compound.

3. The method as defined in claim 1, wherein the surface of the article is sprayed with said organophosphorus compound.

4. The method as defined in claim 1, wherein said organophosphorus compound is dry blended with particulate resin prior to forming into said substrate to be plated.

5. The method as defined in claim 1, wherein the surface of said substrate is treated with said organophosphorus compound for 5–20 minutes.

6. In the method of electroless deposition of a metal on an aliphatic polyolefinic substrate which includes the steps of chemically etching, sensitizing, and chemically reducing a salt of said metal onto the surface of said substrate, the improvement which comprises treating the surface of said substrate prior to chemically etching said surface with an organophosphorus compound of the group consisting of: octyl diphenyl phosphite, tridecyl phosphite, triphenyl phosphite, phenyl didecyl phosphite, decyl diphenyl phosphite, trilauryl thiophosphite, dioctyl hydrogen phosphite, tetraphenyl di(propyleneoxy) diphosphite, decyl phenyl decanephosphonate, tri(butoxyethyl) phosphate, tri-iso-octyl phosphate, tetra(nonylphenyl) poly(propyleneoxy) diphosphite, triethyl phosphite, triphenyl phosphate, bis(nonylphenyl) phenyl phosphite, and tri(nonylphenyl) phosphite.

7. The method as defined in claim 6, wherein the article is immersed in said organophosphorus compound.

9

8. The method as defined in claim 6, wherein the surface of the article is sprayed with said organophosphorus compound.

9. The method as defined in claim 6, wherein said organophosphorus compound is dry blended with particulate resin prior to forming into said substrate to be plated.

10. The method as defined in claim 6, wherein the surface of said substrate is treated with said organophosphorus compound for 5-20 minutes.

10

References Cited

UNITED STATES PATENTS

3,437,507 4/1969 Jensen ----- 117-160X

5 ALFRED L. LEAVITT, Primary Examiner

J. A. BELL, Assistant Examiner

U.S. Cl. X.R.

10 117-160R; 204-30