RELTEK
Adhesives and Coatings for Harsh Environments

Adhesion, Adhesion Failure,

and

BONDiT™

Bonding System for Metal and Other Minerals to Polymers

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1. Introduction

1.1 Scope

This standard establishes the principles of operation, specifications and procedures for handling and molding to **BONDiT™** coated shells and related equipment.

1.2 Referenced Documents

ASTM D 907-91b
ASTM D 2651-90

1.3 Registered trademarks

BONDiT™ is a trademark. Use of the name is by written permission only.

1.4 Document revision status

REV	Date	Section(s)
-A-	09/01/94	Initial release
-B-	10/17/01	Extract from **BONDiT™** Operations Manual, bound, two-sided printing style
-C-	07/03/03	Updated and bound booklet style
-D-	06/21/06	Revision for Web publishing

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1.5 Contents

2. Definition of Terms[1]

2.1 Absorption; absorb[2]

The process of absorbing or of being absorbed; to take in and make part of an existent whole.

2.2 Adherend

A body held to another body by an adhesive.

2.3 Adhesion

The state in which two surfaces are held together by interfacial forces which may consist of valence forces or interlocking action, or both.

Mechanical adhesion: adhesion between surfaces in which the adhesive holds the parts together by interlocking action.

Specific adhesion: adhesion between surfaces which are held together by valence forces of the same type as those which give rise to cohesion.

2.4 Adhesive

A substance capable of holding materials together by surface attachment.

2.5 Adhesive bond failure

Rupture of an adhesive bond, such that the separation appears to be at the adhesive adherend interface.

2.6 Adsorption; adsorb[3]

The adhesion in an extremely thin layer of molecules (as of gases and liquids) to the surfaces of solid bodies or liquids with which they are in contact.

2.7 Bulk adherend

As related to interphase, the portion of adherend, unaltered by inter action with the adhesive.

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2.8 Bulk adhesive

As related to interphase, the portion of adhesive, unaltered by inter action with the adherend.

2.9 Bulk failure[4]

Rupture of an adhesive bond, such that the separation appears to be in the bulk adherend.

2.10 Chemisorption

A chemical reaction between the substrate or adherend and the adhesive such that the adhesive is effectively absorbed by chemical bonds, and together a new chemical blend is formed in the interfacial region, yet, the identities of the forming parts are clearly distinguishable. In the context of adhesion this is in contrast to physical adsorption or hydrogen bonding. In polymer to metal adhesion chemisorption commonly occurs via an oxane bond between the metal substrate and the polymer.

2.11 Cohesion

The state in which the particles of a single substance are held together by primary or secondary valence forces. As used in the adhesive field, the state in which the particles of the adhesive (or adherend) are held together by these forces.

2.12 Cohesive bond failure

Rupture of an adhesive bond, such that the separation appears to be within the adhesive.

2.13 Contact-Angle Test

Wettability may also be determined by measuring the contact angle between the polymer surface and a drop of a reference liquid, such as distilled water. A small contact angle indicates that the liquid is wetting the polymer effectively, while large contact angles show that the wetting is poor.[5]

2.14 Dispersion Forces

See van der Waal's forces.

2.15 Hydrogen Bonding

Hydrogen bonding results from the attraction of a positive hydrogen atom of one molecule, such as water, for some of the electrons of an oxygen atom of a second molecule, such as another water molecule. That is what makes water molecules stay close together and form a liquid instead of a gas. Alcohol is another example of hydrogen bonding similar to water. Hydrogen bonding also occurs between water and metal Oxides. It is also referred to as the hydrogen Bridge. Although the hydrogen bond is stronger than the van der Waal's attraction between two molecules, it is not so strong as an electrovalent or a covalent bond.[6]

2.16 Hydrophilic[7]

Having a strong affinity for water.

2.17 Hydrophobic[8]

Lacking affinity for water.

2.18 Interphase

In an adhesive joint, a region of finite dimension extending from a point in the adherend where the local properties (chemical, physical, mechanical, and morphological, either singly or in any combination) begin to change from the bulk properties, through the interface, and into the adhesive up to a point where the local properties equal the properties of the adhesive.

2.19 Interphase failure[9]

Rupture of an adhesive bond, such that the separation appears to be within the interphase region.

2.20 Primer[10]

A coating applied to a surface, prior to the application of an adhesive, to improve the performance of the bond. An adhesive primer is usually a dilute solution of an adhesive in an organic solvent applied to a dried film thickness of 0.00006 to 0.002 inch. Some of its functions include: improve wetting, protect the adherend surface from oxidation after cleaning, extending the time that may elapse between surface preparation and adhesive application, help inhibit corrosion, modify the properties of the adhesive to improve certain characteristics, such as peel strength; serve as a barrier coat to prevent unfavorable reactions between adhesive and adherend; hold adhesive films or adherend in place during assembly, this type of primer retains tack, or develops tack at room or elevated temperatures.

The use of primers provides (1) more flexible manufacturing scheduling, (2) high reliability of joints, (3) less rigorous cure conditions, (4) wider latitude in choice of adhesive system, and (5) more durable joints. Primers are usually not fully cured during their initial application. They are dried at room temperature and some are force-dried for 30 to 60 minutes at 150°F. These steps, frequently called "flashing"' provide a dry non-tacky surface which can be protected form contamination and physical damage by wrapping with clean paper, sealing in polyethylene bags, or covering with a nontransferring adhesive-backed paper.

2.21 Substrate

As related to adhesives, a material upon which an adhesive is applied, typically metal.

2.22 van der Waal's forces[11]

Attractive forces due to physical adsorption. These include molecules with permanent dipoles (i.e. water on metal oxides), dipoles induced by permanent dipoles in neighboring molecules (water on some polymers), dispersion forces which are dipoles produced by the motion of electrons within the molecule and are independent of the polarity or lack of polarity of the molecule. These bonds are more than sufficient to produce bonds stronger than the cohesive strength of most materials used as adhesives. Dispersion forces are usually considered to be the major attractive force even in the presence of polar groups and hydrogen bonding groups.

2.23 Wetting[12]

> The process in which a liquid spontaneously adheres to and spreads on a solid surface. A surface is said to be completely wet by a liquid if the contact angle is zero, and incompletely wet if it is a finite angle. Surfaces are commonly regarded as unwettable if the angle exceeds 90 degrees.

2.24 Water-Break Test[13]

> This test depends on the observation that a clean surface (one that is chemically active or polar) will hold a continuous film of water, rather than a series of isolated droplets. This is known as a water-break-free condition.

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3. BONDiT™ System Description

3.1 Introduction

Bonding of organic polymers to inorganic surfaces is hardly new technology. The Sumerians and Babylonians used asphalt and pitch for floor covering and paving. Naturally occurring polymers were used by the ancient Egyptians to varnish their sarcophagi. The 1940 evolution of composite plastics filled with glass fiber (mineral) for structural material replacement of aluminum and steel brought on the discovery of another phenomenon. Prolonged exposure to moisture severely degraded the composite's strength-to-weight ratio. The loss of strength demonstrated the power of intruding water to debond resin from hydrophilic glass.

The same phenomenon has been confronted in many other circumstances, particularly in under sea applications where organic polymers moldings and coatings debond from metals. The past fifteen years of naval experience reveals susceptibility of bonded materials onboard ship where electrical connectors fail because of overmold polymers debonding. Current studies attribute cathodic action between the connector shell in the electrolytic ocean water and ship hull sacrificial zinc plates as a major contributor to the failure. Researchers are in agreement that water with high alkalinity, resulting from the cathodic action, attacks the polymer/metal bond interface.

Polymer to polymer bonds can be made inherently moisture resistant in a variety of ways, particularly by diffusion of the polymers into each other physical absorption as apposed to chemisorption which does not rely on chemical reaction. Metal to polymer bonds, which cannot absorb each other, are inherently not moisture resistant and are limited in methods to achieve moisture resistance.

After fifty years of intensive study debate continues on the mechanism of adhesion between polymers and metals. In spite of the debate, some aspects have become rather clear and generally accepted. Recent studies lead to the realization that polymer/metal bonds will hydrolyze in the presence of moisture, and consequential debonding cannot be stopped. High Ph environments, such as a consequence of cathodic action in the environs of ship hulls, especially aggravate the condition. In addition, thermal shocking is found to be a major factor in

debonding. Research has developed a better understanding of the mechanism. The product derived from that research, **BONDiT™**, is a reliable metal to polymer bonding system able to withstand long service in continuously submerged ocean environments, subjected to caustic chemical attack by cathodic action and thermal shocks.

3.2 How Does Adhesion Work?

From the ASTM Book of Standards Adhesion is defined as "the holding together of two surfaces by interfacial forces which may consist of valence forces or interlocking action, or both." An *adhesive* is "a substance capable of holding materials together by surface attachment," and an *adherend* is "a body which is held to another body by an adhesive." (See Definition of Terms, Sections 0, 0, and 0.)

In order to bond to a surface, an adhesive must first wet and spread on that surface. This means that the surface tension of the adhesive should be less than the *free surface energy* or *critical surface tension* of the *adherend*. Since the free surface energy of most solids is much higher than that of liquids, and the lowering of the free surface energy by adsorbed material (such as oxygen) is correspondingly much greater than in liquids (such as a primer), then *contamination of the adherend surface can greatly reduce wetting by the adhesive*. For instance, the *free surface energy* of mica when cleaved in a vacuum is 4,500 ergs/cm^2, but when cleaved in air the free surface energy is only 375 ergs/cm^2.[14] Typical *surface tension* of solid polar materials ranges from 100 to 3000 ergs/cm^2. Organic liquids and water have *surface free energies* of less than 100 ergs/cm^2. Some authors believe *dispersion forces* are to be considered the major attractive force even in the presence of polar groups and *hydrogen bonding* groups.[15]

Obviously, preparation of a clean, high energy surface is mandatory for good bonding. As one researcher puts it, "results demonstrate that the surface treatment forming a high energy surface is the basic contributory factor in improving adhesion."[16] A clean metal surface is defined by ASTM D2651-90, Section 5.5.4. Such a surface is polar in that it would normally have a *controlled oxidized surface after treatment*, and since the final cleaning would include a water rinse, the surface would include an adsorbed layer or layers of water. Wiping with an organic solvent would then, be a contamination since it results in a finite contact angle of water for that surface, as compared to a zero contact angle prescribed per ASTM D2651-90.

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In order for two substances to interact directly, the molecules of one must come within a few Angstroms of those of the other, i.e., the liquid must *adsorb* onto the solid surface. This is an exothermic process.[17] During the wetting action of the primer with mineral substrate *physical adsorption* takes place, followed by *hydrogen bonding* and then by *chemisorption* and chemical reaction. Physical adsorption is dominated by *van der Waal's* forces while chemisorption is dominated by valence forces. Although somewhat arbitrary, it has been stated that interactions up to 10 kcal/mole are considered physical adsorption, while those greater than 10 kcal/mole are regarded as chemisorption.[18] Van der Waal's forces are derived from molecular dipoles of various kinds, and are short range. *Dispersion forces* are dipoles produced by the motion of electrons within the molecule and are independent of the polarity or lack of polarity of the molecules. The distinction between *chemisorption* and chemical reaction is the retention of chemical identity of the interacting species, which may be recovered intact by supplying *desorption* energy in the case of *chemisorption*, while this is not generally possible in the case of chemical reaction.[19] Chemisorption is particularly important in the equilibrium state believed to exist between bonding agents and mineral substrate where the equilibrium constants govern the quality of bonding. It has been argued that bonds due to *chemisorption* are far superior in terms of durability in the presence of an aqueous environment.[20]

As stated the clean *hydrophilic* polar mineral surfaces in equilibrium with the atmosphere (achieved very rapidly in most cases) will have at least a monolayer of water (HO^-, H_2O, H_3O^+).[21] (A transition layer of weak metal oxides will form in a short time.) In contrast to the importance of a clean substrate surface, the existence of the water layer will inhibit the adhesion of nonpolar polymers, such as polyethylene. By adding bonding agents to the polymer the water can form reactions with bonding agents such as carboxyl groups to condense the bonding agent onto the metal in a chemisorbed bonds. Study leads to the conclusion that for polar substrate the reactivity of the coupler or bonding agent is of much greater significance than polarity or wettability of the substrate surface.

Some of the more moisture resistant chemisorbed bonds require energy in the form of heat to complete the chemisorption of the adhesive/coupler. The heat and pressure (and motion in the case of molding processes) induce intimate contact at the interface of the mineral and polymer, reduce the surface tension of the polymer and facilitate wetting and chemical reaction with the

substrate. (Motion of the polymer relative to the substrate may also contribute to preferential orientation of the polymer molecule to the substrate, scrub contaminates free from the substrate, and consequently improve adhesion.) *Without heat and pressure to cause the adhesive to wet, spread, and adsorb to the adherend, no appreciable adhesion results.*

Other mechanisms of adhesion have been discussed in many forms. Mineral substrate are often etched or abraded to heighten mechanical interlocking of polymer to substrate. Bikerman[22] views surface roughness as making a primary contribution to adhesion. Other authors dispute this position to varying degrees as being only a contributing factor to actually degrading the quality of chemisorption.[23] [24]

The diffusion theory attributes adhesion to the ability of organic molecules to diffuse into each other. It has been well argued that "diffusion is considered contributory only in adhesive-adherend combinations where some degree of mutual solubility exists. This would occur primarily in the bonding of thermoplastic materials."[25] However, practice has demonstrated that diffusion of bonding agents between polymers is very important to moisture resistance of dissimilar polymer adhesion.
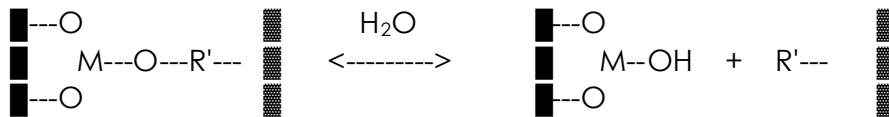
3.3 Adhesion Failure

The are two kinds of adhesion failure commonly defined as: adhesive failure - "rupture of an adhesive bond, such that the plane of separation appears to be at the adhesive-adherend interface," cohesive failure - "rupture of an adhesive bond, such that the separation appears to be within the adhesive." Two additional useful definitions are: *interphase failure* - rupture of an adhesive bond, such that the separation appears to be within the *interphase region*; *bulk failure* - rupture of an adhesive bond, such that the separation appears to be in the *bulk adherend*.

Assuming a good bond initially, there are two basic contributors to adhesion failure: polymer/substrate interface stresses, and water desorption. In practice these work together to reduce a cohesive bond to adhesive failure.

It is well established that moisture will travel through a polymer to reach the interface, and by diffusion along the interface. The diffusion along the interface is as much as four hundred fifty times faster than through the polymer.[26] However, depending on geometry and material, moisture may saturate the polymer and fill the interfacial region faster than moisture flow along the interface.

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Typical polymer saturation ranges widely from 0.015% to 24% of mass, while the interfacial region saturation is relatively constant at 3.0% to 3.5% of surface area regardless of the polymer or mineral surface, the hydrophilic nature of the mineral surface being the biggest determinant.

There is little doubt a saturated interface will *hydrolyze* the polymer/metal bonds. However, the reaction is reversible, and hence, if the interface is dried, the bonds will return to their former state (ignoring contaminants.) The normal state of equilibrium in the moisture environment is a percentage of each side of the equation exists, with individual metal/polymer bonds having some probability of being in either state. State variables determine the probability, and correspondingly which side of the equation is favored. In any case, some percentage of debonding will exist--its unavoidable.

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█---O                  ▓           H₂O         █---O                              ▓
█    M---O---R'---      ▓    <--------->        █    M--OH    +    R'---          ▓
█---O                  ▓                        █---O                              ▓
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R' = Primer / adhesive coating
M--O = Metal oxide
OH = Hydroxyl ion
█ = Metal substrate
▓ = Polymer overmold

Variables such as, activation energies, bond temperature, bond chemical structure and Ph of the water have significant effects on the probability.

In and of itself, the equilibrium bond conditions may be satisfactory for the application. Bond failure will occur only when the interfacial region is separated beyond the range that dispersion forces can act to induce chemisorption. Thermal stress would be the most significant of the mechanical stresses in a typical application. Polymer coefficients of thermal expansion range from two times to twenty times that of common metals. For polymers having adequate bond density this does not pose a problem, baring actual fracture of the bulk material. However, with a

lowered bond density resulting from hydrolysis of the interfacial region the thermal expansion of the polymer causes the polymer to physically break away from the metal interface, thereby, permanently breaking the bond.

Another factor causing stress is swelling due to moisture absorption by the polymer. The degree of swelling is dependent on the nature of the polymer: polyurethane having very hydrophilic qualities, and polyethylene very low, i.e. hydrophobic. Since the metallic substrate will not swell the adhesive-substrate interface is the plane of discontinuity and resulting stress build-up. When this accompanies desorption by water (hydrolyzation of the adhesive bond) and thermal shock in a physically adsorbed adhesive, then failure in adhesion maybe inevitable.[27]

The cathodic environment increases the available OH^- ions at the exposed edges of the interface. That moves the equilibrium point of the reaction in favor of debonding. Further increase in the pH moves the equilibrium constants so far in favor of debonding that virtually no organic/mineral interface can withstand the chemical attack. Any mechanical stress at that "loose" edge will begin complete debonding of the polymer from the mineral substrate. Blistering is the same effect, commonly seen in paint on metal substrate. As the moisture penetrates through the polymer to the hydrophilic metal surface, microscopic irregularities and contaminates offer sites on the metal surface to form oxidation-reduction reactions. That liberates OH^- ions; the continuation of which increases the pH level to very high levels. That in turn increases the rate of hydrolyzation of the polymer/metal interface and the blister spreads, further exposing metal that can react, ultimately delaminating the polymer completely.

3.4 BONDiT™ System Description

BONDiT™ is a multicomponent system to provide high moisture resistant metal to polymer bonds. It provides a moisture and thermal shock resistant substrate for a wide range of polymers, as a tie coating to metal substrate. It is designed with constants that greatly favor the bonding side of the chemical equation. The constants of the individual polymer/metal bond give it a probability 10^4 greater than commonly in use today. It is designed to also reduce the moisture concentration significantly at the interface, and consequently move the equilibrium constants in favor of bonding. The **BONDiT™** system is designed to "manage" thermal stresses and provide a balanced transition from rigid metal to high expansion polymers, such as polyurethanes.

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Accelerated Life Tests demonstrate bond survival rate improvements of 3,000% over common systems in use today. In all cases the bulk adherend failed under adhesion pull tests, before and after accelerated aging, with such overmold materials as polyurethane, neoprene, and LDPE.

The entire system works together to provide a reliable bond between the metal substrate and the overmolded polymer. The **BONDiT™** system is proven to withstand and environment of moisture, cathodically active conditions and thermal and mechanical stress.

3.5 BONDiT™ Technical Specifications

Normal operating temperatures for **BONDiT™** are -50°F to 350°F. **BONDiT™** will maintain adhesion to metal substrate up to temperatures of 400°F in super heated water or steam, and certain oils. However, above 300°F, **BONDiT™** begins to soften. From 350°F the **BONDiT™** to metal bond becomes increasingly weaker such that it may be pried loose by mechanical means.

4. Testing

4.1 Water-Break-Free Test[28]

4.1.1 Definition:

The term "water-break-free" is used extensively in conjunction with cleaning for adhesive bonding. It is a check of the surface tension of the substrate that is to be joined. This test depends on the observation that a clean surface (one that is chemically active or polar) will hold a continuous film of water, rather than a series of isolated droplets. This is known as a water-break-free condition. A break in the water film indicates a soiled or contaminated area.

4.1.2 Procedure

Distilled water should be used for this test and may be applied with an eye dropper or the equivalent. A drainage time of about 30 seconds should be allowed. Care should be taken to ensure any cleaning compound or fluid is washed clean with distilled water as the final wash. Left over cleaning compounds will yield an erroneous evaluation. Wipe the surface dry with lint free cloth like Kimwipes.

4.1.3 Evaluation

If the metal surface is not properly cleaned the water will not spread when placed on the surface. If the surface is clean and surface tension low, the water will spread naturally, wetting a large area.

If a water-break-free condition is not observed on the treated surface, it should not be used for bonding. The surface should be recleaned until the test is passed. If continued failures occur, the treating process itself should be analyzed to determine the cause of the problem.[29]

Tests show a cleaned metal surface will oxidize to the point of non-usability within 15 minutes in ambient air, and hence, require recleaning.

4.2 Contact-Angle Test

Wettability may also be determined by measuring the contact angle between the polymer surface and a drop of a reference liquid, such as distilled water. A small contact angle indicates that the liquid is wetting the polymer effectively, while large contact angles show that the wetting is poor. Every surface has a critical surface tension, γ_c, of wetting. Liquids with surface-free energies below γ_c will have finite contact angles. The critical surface tension is in units of dyne/cm at 20°C. Contact angles for untreated materials vary from 37° to 48° for relatively polar materials such as nylon to highs of 100° and 97° for the nonpolar, unbondable silicone and polyethylene resins.[30]

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5. End Notes

1. ASTM 907-91b unless otherwise noted.

2. Webster's Ninth New Collegiate Dictionary.

3. Webster's Ninth New Collegiate Dictionary.

4. Not a standard term.   Used in this context to enhance technical description.

5. Landrock, Arthur H., *Adhesives Technology Handbook*, Noyes Publications, Park Ridge, N.J., 1985, pg. 63.

6. Keenan, Charles W.; *General College Chemistry*, Harper & Row, N.Y., second edition, pg. 139.

7. Webster's Ninth New Collegiate Dictionary

8. Webster's Ninth New Collegiate Dictionary

9. Not a standard term. Created to provide enhanced technical description.

10. Landrock, pg. 61.

11. De Lollis, Nicholas J., *Adhesives, Adherends, Adhesion*; Robert E. Krieger Publishing Co., Malabar, Florida, 1985. Pg. 13-15.

12. Landrock, pg. 29.

13. ASTM D 2651 par 5.5.4.

14. E. U. Condon, *Handbook of Physics*, McGraw-Hill, 1958, pgs. 5-9.

15. DeLollis, pg. 13.

16. DeLollis, pg. 21.   Reprint of 2nd chapter in *Handbook of Adhesive Bonding*, by C. V. Cagle, Editor, 1973 by McGraw-Hill Inc., which is out of print.

17. Gent, A. N., and Hamed, G. R. "Fundamentals of Adhesion." In *Handbook of Adhesives*, edited by I. Skeists. New York: Van Nostrand Reinhold Publishing, 1990; Pg. 44.

18. Gent, pg. 42.

19. Gent, pg. 42.

20. De Lollis, pg. 14.

21. Gent, pg. 45.

22. Bikerman, J. J., "The Fundamentals of Tackiness and Adhesion," *J. Coloid 2*, 174 (1947).

23. Cagle, C. V. "Adhesion Theory Review and Critique." In *Adhesives, Adherends, Adhesion* by N. J. De Lollis, pg. 17. "...inherent roughness means inherent voids due to incomplete wetting and to incomplete desorption." The same author also cites trapped gas bubbles and imperfect molecular fit as negative factors, presented in works of N. A. DeBruyne and D. D. Eley.

24. Lee & Neville, *Handbook of Epoxy Resins*. New York: McGraw-Hill Book Company, Inc., 1982 Reissue, pg. 21-16. "The question of whether or not a smooth surface is preferred for metals is still not answered. Evidence is available on both sides. A rough surface theoretically increases the bonding area and provides for some degree of mechanical adhesion. On the other hand, improved wetting may be obtained with a smooth surface,...studies using an ultra-centrifuge appear to confirm the superiority of smooth steel surfaces over rough ones."

25. Cagle, pg. 18.

26. De Lollis, pg. 23. Report of J.A. Laird, "Glass Surface Chemistry for Glass Fiber Reinforced Plastics," Final Report, Navy Contract No. W-0679-C(FBM), June 1963.

27. De Lollis, pg. 29.

28. ASTM D 2651 par 5.5.4.

29. Landrock, Page 63

30. Landrock, page 63.

6. Notes