ARTNERS PRESERVING OUR PAST, PLANNING OUR FUTURE

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UNDERSTANDING CYANOACRYLATE ADHESIVES AND CONSOLIDANTS AND THEIR USE IN VERTEBRATE PALEONTOLOGY

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ABSTRACT--Under ideal conditions, vertebrate fossils should be conserved without applying chemicals to the specimens. If this is not possible, as is often the case, and scientific information will be lost without the use of chemicals, then educated decisions must be made. Familiarity with the uses and properties of a wide variety of adhesives and consolidants will improve the decision making process.

Cyanoacrylates (known generically as superglues) are water-thin, organic liquids. Developed for other industries, they were first used to conserve vertebrate fossils in the 1980s. Interest in these easy-to-use, quick-to-cure adhesives has increased. Today they are routinely referenced in fossil preparation literature.

The chemistry and properties of various viscosities of cyanoacrylates are discussed, as well as effective usage. Both pure ethyl cyanoacrylate and ethyl cyanoacrylate with poly (methyl methacrylate) harden by means of anionic polymerization that is initiated by the presence of a weak base. Long chain-like molecules form until all of the material is hardened or an acid terminates the process. Adhesive bonds of cyanoacrylate can be broken (reversed) with overnight exposure to one of four solvents. In general, thin, pure ethyl cyanoacrylates are best used as consolidants. Pure ethyl cyanoacrylates penetrate deeply into porous bone and have high tensile strength. Though brittleness increases with time (suggesting poor aging properties), use as a consolidant minimizes these drawbacks. Thicker ethyl cyanoacrylates containing poly (methyl methacrylates) are best used as adhesives because of their strength, improved aging properties, and ability to more evenly coat bond lines.

HISTORY

As with many compounds used in the conservation of vertebrate fossils, cyanoacrylates were developed for use in other industries. The earliest patents on cyanoacrylates were issued in 1949 to Alan Ardis and assigned to the B.F. Goodrich Company. His patents refer to the use of cyanoacrylates for the production of "hard, clear, glass-like resins," which were obtained by heating the compound (Wells, 1981). Throughout the 1950s, 1960s and 1970s, a number of other patents were issued to the Research Laboratories of Eastman Kodak, and later to Johnson and Johnson and Japanese entrepreneurs as the adhesive qualities of cyanoacrylates were refined to produce a general-purpose glue. Popular for its short cure time, it was most often used for bonding small parts that were hard to clamp. Other uses were found in the medical field with much research being conducted on the repair of soft tissues using cyanoacrylates (Wells, 1981). It was not until the 1980s that references could be found relating to the use of cyanoacrylates in fossil conservation (Howie, 1984; Horie, 1987). These early accounts record a growing interest in cyanoacrylates for fossil preparation because of their ease of use and quick cure time. The disadvantages of these products were also recognized early on with concern expressed regarding the difficulty of removing the hardened compound and uncertain aging characteristics.

By the 1990s, the mention of cyanoacrylates began appearing regularly in publications dealing with fossil preparation (Amaral, 1994; Shelton and Chaney, 1994; Howie, 1995; Lindsay, 1995; Shelton and Johnson, 1995; Madsen, 1996; Elder et al., 1997). Today, cyanoacrylates are generally recognized as strong, easy to use, fast curing adhesives with questionable reversibility and uncertain aging characteristics. Lack of impartial physical testing by conservation agencies such as the Canadian Conservation Institute and the Getty Conservation Institute makes it difficult to describe cyanoacrylates in more definitive terms. This lack of impartial data is widely recognized and has split the paleontological community into those who believe that they should not be used until testing is done, and those who believe that the benefits of their use outweigh the unknowns.

CHEMISTRY

Though few of us have an in-depth understanding of chemistry, a rudimentary understanding is necessary to make informed decisions about the numerous preservatives available today. Therefore, a brief digression into organic chemistry is appropriate.

Cyanoacrylates are water-thin, organic liquids. Those available on the market today are usually ethyl cyanoacrylates. Their chemical structure can be seen in Fig 1. Ethyl cyanoacrylates are highly reactive and harden (polymerize) quickly by means of anionic polymerization at room temperature in the presence of a weak base (Coover et al., 1990). Even the base found in moisture (hydroxyl group) is sufficient to initiate the reaction. The entire polymerization reaction proceeds in three steps forming a long, chain-like molecule. Polymerization continues until the reaction is terminated by an acid (Coover et al., 1990) (Fig 2). Stronger bases, as found in prepared activators or accelerators, will make the reaction proceed even more quickly. Because polymerization begins at the point where the liquid contacts a weak base and proceeds back towards the center of the adhesive layer, hardening is not dependent on evaporation as with solvent based adhesives (such as Butvar B-76). Therefore, cyanoacrylates will harden completely even if the glue on the surface of a treated bone polymerizes before the glue deep within the substrate.

The presence of acids on the substrate will inhibit or retard the polymerization process and therefore may require the use of an accelerator. Likewise, acids are used to keep cyanoacrylate liquids from hardening during storage. The type and amount of acid will affect the shelf life (increase it), but at the same time will retard the cure rate when the product is used. The amount of acid has no effect on the resulting strength of the polymer.

Cyanoacrylates come in a variety of viscosities. They are made thicker by dissolving an additional polymer in the liquid ethyl cyanoacrylate. In most cases the polymer is poly (methyl methacrylate). Cyanoacrylates that have the viscosity of petroleum jelly usually contain hydrophobic silicas as well as poly (methyl methacrylates).

To make educated decisions concerning when and where to use cyanoacrylates in fossil conservation, one must know the chemical composition of the specific brand of adhesive at hand. Manufacturers of

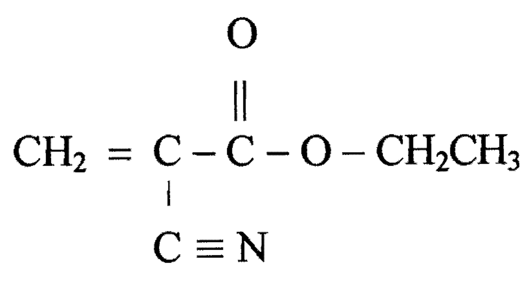

FIGURE 1 - Chemical structure of ethyl cyanoacrylate. C (carbon), H (hydrogen), O (oxygen), N (nitrogen), - (single bond), = (double bond), ≡ (triple bond), 2 (two atoms), 3 (three atoms).

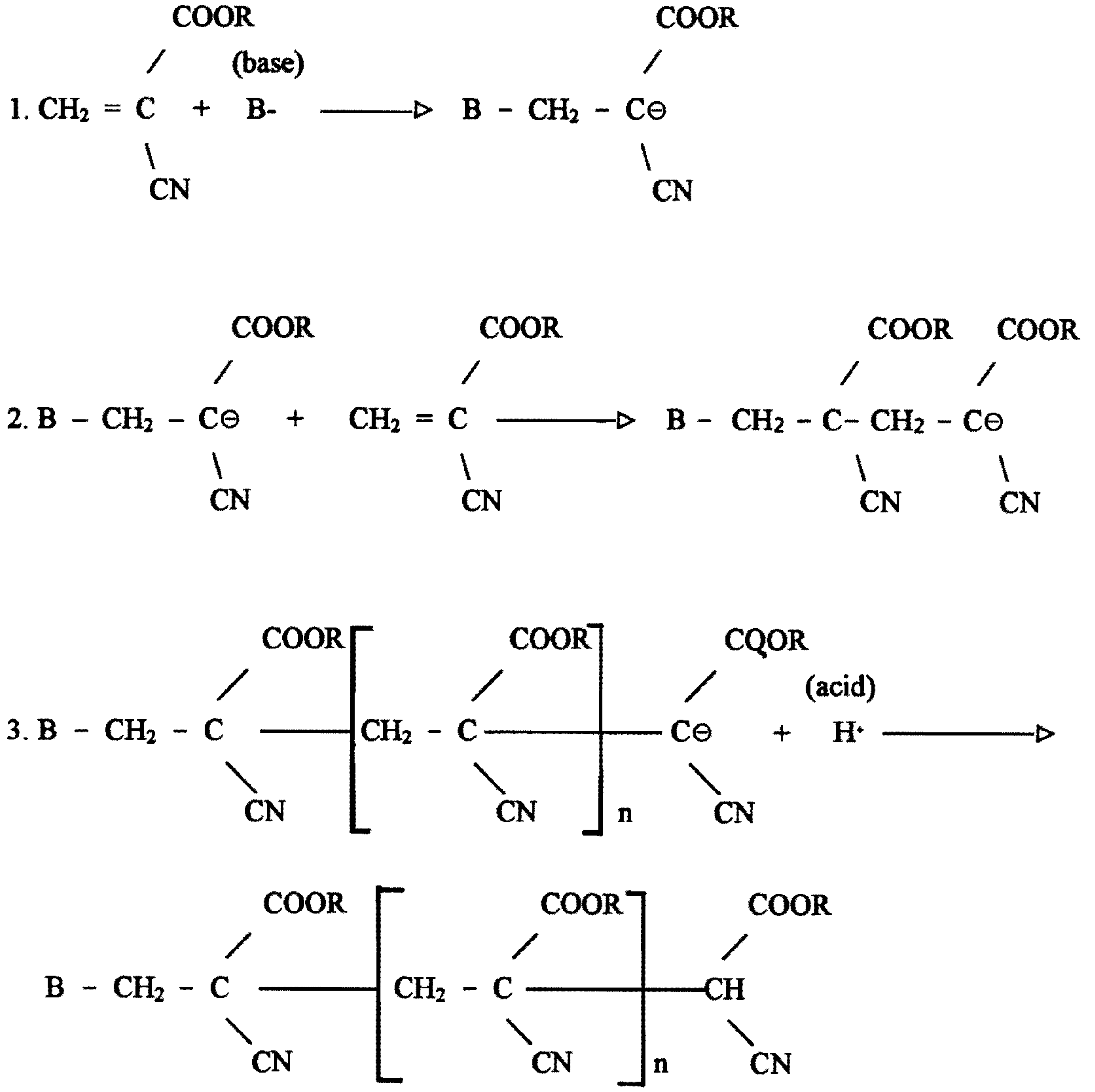

FIGURE 2 - Three step curing mechanism (anionic polymerization) for cyanoacrylates. A weak base initiates polymerization (step 1). Polymerization proceeds as in step 2 until a long, chain-like molecule, called a polymer, is formed. The reaction proceeds until all liquid has hardened, or until an acid (step 3) terminates it. C (carbon), H (hydrogen), O (oxygen), N (nitrogen), B (base), R (variable group), n (large number of repeating units).

cyanoacrylates (and other adhesives) are required to provide Material Safety Data Sheets (MSDS) upon request. Though these sheets will not describe special proprietary formulas, they will state the percentage of basic ingredients such as ethyl cyanoacrylate and poly (methyl methacrylate). These sheets also provide a variety of health and safety information and are essential for any lab.

PROPERTIES

The properties of thin, ethyl cyanoacrylates are much different from those of ethyl cyanoacrylates thickened with some percentage of poly (methyl methacrylate). Therefore, the two groups will be discussed separately.

Pure ethyl cyanoacrylate penetrates deeply into porous substrates. It does not deeply penetrate non-porous substrates. When used to glue two, non-porous pieces together, the bond has very high tensile strength (reaching full strength after 8-24 hours) but is brittle and has low impact and peel strength (Coover et al., 1990). In other words, the strength of the bond varies drastically depending on the direction in which stress is applied. The brittleness continues to increase with time, suggesting that long-term durability is not good. Heat increases the brittleness. Temperature and humidity cycling resistance is poor as well (Coover et al., 1990).

Thicker cyanoacrylates, which are a mixture of ethyl cyanoacrylate and poly (methyl methacrylate), have additional useful properties. Cyanoacrylates composed of as little as 5-10% poly (methyl methacrylate) are reported to have twice the impact strength of thin, pure ethyl cyanoacrylates, as well as increased peel strength (Coover et al., 1990). This decrease in brittleness suggests that the thicker cyanoacrylates will not degrade with time as readily as thin, pure ethyl cyanoacrylates, though analytical testing has not been done on either group of compounds to quantify aging properties.

Bonds of both the thin and thick cyanoacrylates can be weakened or dissolved slowly with various solvents. The adhesive bonds will be destroyed overnight by immersion in either dimethylformamide, nitromethane, dimethyl sulfoxide, or aceto-nitrile (Pollar, 1981). Off-the-shelf cyanoacrylate solvents generally contain one of these solvents. Adhesive bonds will also be destroyed with extended immersion in methanol, acetone, or aqueous acids or alkalis (Pollar, 1981).

EFFECTIVE USAGE

No discussion on the usage of a specific adhesive or consolidant in fossil conservation is appropriate without first addressing their general use. In striving for the ideal situation, it is best to conserve vertebrate fossils without applying any chemicals. This "dry preparation" decreases the possibility that future data will not be able to be extracted from a particular specimen because of chemical contamination. Though some would argue that many solvent based adhesives and consolidants are reversible, it is the assertion of the authors that applying any chemical affects the fossil on a molecular level. Adhesive bonds can be broken, but no compound is completely reversible on the molecular level. As one colleague so aptly put it, reversing a glue applied to a bone is like trying to remove water from a soggy sponge without being able to squeeze it.

If the ideal situation cannot be obtained and scientific information will be lost without the use of chemicals, then, well-informed decisions must be made. Every conservation situation is unique. Sweeping generalizations (common in fossil preparation), such as "no glue should be used which is stronger than the specimen" or "all glues should be reversible" must be abandoned in favor of closely evaluating each individual situation with an open mind. If an adhesive is called for, those who know how to use the greatest variety of adhesives have the most options and will therefore make better decisions.

Pure ethyl cyanoacrylates work best as consolidants. They penetrate well into porous substrates, cure completely even if the surface cures first, and are very strong. Deepest penetration occurs when the cyanoacrylate is left to cure as slowly as possible, without the aid of an accelerator. When used as a consolidant rather than as an adhesive, brittleness and resistance to mechanical force may become a relatively unimportant consideration. If the fossil surface is not porous, thin cyanoacrylates form a sheet over the specimen that can usually be pealed off after hardening. This type of usage has field applications, though again, every situation is unique. As with any chemical, one should test it on an insignificant fossil fragment to be sure that the desired results are achieved.

Thicker cyanoacrylates work best as adhesives because they are less brittle, have better long-term aging characteristics, and more evenly coat bond lines than do thin, pure ethyl cyanoacrylates. Cyanoacrylates in general form stronger bonds when bonding non-porous surfaces. Because bone surfaces are usually porous, to achieve a strong bond, porous surfaces need to be changed to non-porous ones. This can be accomplished by first using a thin cyanoacrylate as a consolidant on the two broken surfaces, letting the surfaces dry, and then using a thicker cyanoacrylate to glue the two surfaces. Choosing the correct thickness of cyanoacrylate is very important and is dependent on the size of the pieces being glued and how tightly the two surfaces fit together. Because as little as 5-10% poly (methyl methacrylate) increases aging properties and decreases brittleness, it is not always necessary to use the thickest possible adhesive. Consult the MSDS for specific percentages.

Accelerators or activators should be used sparingly. They should be used to initiate the hardening process for a specific purpose (to stop penetration at a particular point for instance), not as a replacement for patience. Accelerators can cause staining when they come in contact with certain iron-rich minerals and are highly reactive when exposed to wide temperature fluctuations as can occur in fieldwork.

Cyanoacrylate bonds can be reversed (broken) with prolonged exposure to dimethylformamide, nitro-methane, dimethyl sulfoxide, and aceto-nitrile (Pollar, 1981). These compounds are marketed as cyanoacrylate solvents under a variety of names, depending on the company. As is the case with solvent-based glues, successfully reversing a bond is heavily dependent on being able to get the solvent to the adhesive. All too frequently in fossil conservation solvents can only be applied to the surface of the adhesive. It then becomes a slow (and often repetitive) process of allowing the solvent to turn the surface adhesive gummy, removing the gummy adhesive mechanically, and then applying more solvent. Preliminary tests comparing cyanoacrylates to solvent-based Butvar B-76 suggests that both are equally "reversible" under these conditions.

Because cyanoacrylates begin to harden in the presence of a weak base, such as is found in moisture, they can not be used effectively in damp areas. Likewise, once a bottle of liquid cyanoacrylate is open, it should not be exposed to wide temperature fluctuations, which can cause condensation to collect in the container. Unopened cyanoacrylate should be stored at freezing temperatures to prolong shelf life, though liquid cyanoacrylate should be allowed to warm to room temperature before using.

CONCLUSIONS

Vertebrate fossils are best conserved without the application of chemicals. If this is not possible and an adhesive or consolidant is necessary, then educated, well-informed decisions must be made. Gone are the days when decisions could be based exclusively on what had been used before. Today, a basic understanding of the chemistry and properties of adhesives is required to make good decisions.

Cyanoacrylates are one of many adhesives available to the conservation community. Like all glues, cyanoacrylates have their advantages and disadvantages. Only by understanding their chemistry and properties can they be properly used.

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