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3,133,887

NEUTRON SHIELDS AND METHODS OF MANUFACTURING THEM

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The invention relates to neutron shields and methods of manufacturing them. These are for use in atomic energy plants or in any place where neutrons are released to protect persons and materials that might become radioactive when subjected to neutron bombardment.

One object of the invention is to provide a light weight neutron shield which can be made out of relatively inexpensive material. Another object of the invention is to provide a composition for a neutron shield and a method of manufacture permitting various shapes to be made with accuracy and at reasonable cost. Another object of the invention is to provide a mix in which a large percentage of the neutron shielding element is embodied. Another object of the invention is to provide a method involving a selection of ingredients with the optimum properties and steps for the manufacturing operations permitting expeditious manufacture of neutron shields of complicated shapes serving the purposes of the Atomic Energy Commission and other authorities. Another object of the invention is to provide a neutron shield which is also a good thermal insulator. Another object is to produce a tough neutron shield which can be readily machined and ground to produce a finished shield of accurate dimensions to specifications.

Other objects will be in part obvious or in part pointed out hereinafter.

Boron, as it occurs in nature, has about the highest neutron cross-section per gram of any element. Neutron cross-section means neutron capture cross section and is given in barns. One barn is equal to 10^{-22} square millimeters. One barn is therefore one ten quintillionth of a square millimeter. Boron as found in nature contains about 18.8% of B_{10} isotope with a neutron cross-section of 4020 barns and 81.2% of the isotope B_{11} with a neutron cross-section a little less than .05 barn. It turns out that the normal boron has a neutron capture cross-section of about 756 barns.

The isotope B_{10} is very expensive as is also boron enriched in this isotope. Even ordinary boron is quite expensive. For the neutron shielding material we use boron carbide, the normal "pure" compound of which is B_4C which is a relatively inexpensive material and in the claims this means boron carbide of any ratio of the isotopes. Boron carbide is commercially available from a number of sources of supply with an empirical range of from $B_{2.5}C$ to $B_{5.8}C$ (Norton Company, Worcester, Massachusetts) and we use this material but naturally prefer the high boron boron carbide up to the top limits of boron and when boron carbide with better than $B_{5.8}C$ becomes available, that will be preferred. It is understood, however, that the boron carbide with the higher ratios of boron is more expensive than that with the lower ratios of boron.

Another way of expressing this is that $B_{2.5}C$ is 69.3% boron, B_4C is 78.3% boron, $B_{5.8}C$ is 83.9% boron and $B_{4.3}C$ is 79.5% boron. All these figures assume that the compound or mixture is nothing but boron and carbon. As commercially this is not true, we have used the commercial material which, however, contains less than 2% by weight material other than boron and carbon. Most of this material up to 2% is iron and oxygen which in such proportions are not harmful. We have fixed, for

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the best mode, upon $B_{4.3}C$ or 79.5% of boron to the total boron and carbon because for control we want a uniform material and this can now be readily made up by mixing various high boron boron carbides available. So far as we are aware, the true compound is B_4C although as this is an interstitial compound, it is a matter of scientific choice whether some of the material having more boron than B_4C is still a compound or a mixture, but probably the best opinion is that it is B_4C with boron in solid solution. Where there is an excess of carbon represented by a deficiency of boron below B_4C , the carbon excess occurs as graphite.

We mix the boron carbide in the form of granular material with epoxy resin. The particle size of the boron carbide which we use in the best mode of the invention is shown in Table I.

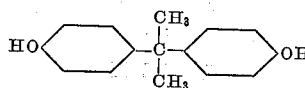
TABLE I

Boron carbide mesh size:	Percentage by weight
46 to 66-----	35
66 to 120-----	45
120 to 325-----	20

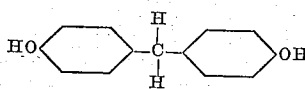
Because of the requirement for machining and grinding to produce shields of the required tolerances, we prefer to avoid particles of large size. This can be set at 20 mesh size as the largest particle size to give the best results. Because of the difficulty of mixing very fine flours with the epoxy resin, we prefer to have nothing but an insignificant proportion, say 2% by weight, smaller than 1200 mesh. As there is no such screen, such particles are settling tank fines. We can have 20% below 600 mesh, 50% below 325 mesh.

The epoxy resins are described by Lee and Neville in a recent book entitled "Epoxy Resins," McGraw Hill, New York and London 1957. While there are many epoxy resins we have found that the satisfactory ones for our purpose are bisphenol A and bisphenol F. These are as follows:

Bisphenol A Monomer



Bisphenol F Monomer

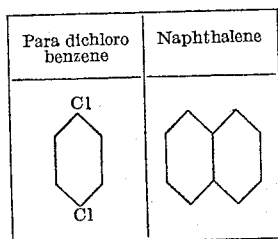


The epoxy resin that we have used is diglyceride ether of bisphenol A. This, of course, is still the monomer. It becomes a resin after having been set by a cross-linking agent sometimes called a hardener. The monomer is a liquid and so is the hardener. These hardeners are usually amines, amides, or organic acid or organic acid anhydrides. They are sometimes called curing agents. When the hardener and the monomer are mixed, the resin starts to set. These epoxy resins, especially those mentioned, are cold setting, that is to say they will set at room temperature. Naturally heat above room temperature accelerates the setting.

The monomer which we have actually used and which we prefer is sold by Ciba, Inc. under the brand Araldite 502. This is a diglyceride of bisphenol A. The hardener which we have used is Rubber and Asbestos' Bondmaster CH44. This is an amine. We have used ten parts of the epoxy monomer to one part of the hardener but do not want to be limited to any particular proportions as that is a matter of resin chemistry. The proportion mentioned is the best mode known to us.

In order to make a light weight shield, we incorporate a large proportion of volatile solid. The most practical

one known to us is para dichloro benzene. This is the best mode and what we have used. Another one is naphthalene. These are related as shown in the following:



Both readily volatilize and both are familiar to people in use as moth balls, but para dichloro benzene has largely superseded naphthalene. This material is incorporated in various proportions depending upon specifications for the shield and as the best mode for many products twice the volume of para dichloro benzene (hereinafter referred to a PDB) of the epoxy mixture and boron carbide is used.

In order to cause green shrinkage and to make the mix more workable, we preferably use an extender such as toluol. This adds more liquid phase without adding more resin which we find desirable. Green shrinkage is desired so as to make it easier to take the green piece out of the mold. This extender also slows down the room temperature setting which is desirable so that the mix will not set in part before it is well tamped. Other extenders could be used such as the ketones including methyl ethyl ketone, ethyl ethyl ketone, acetone and many others. The criterion is that practically all of the extender should evaporate in twenty-four hours at room temperature and toluol and these ketones will do so. They leave practically no residue. All slow down the cure somewhat but have no deleterious effect upon the resin. Any extender will ordinarily be used in small proportions. The shields can be made without the use of any extender at all, but it is more efficient to use one.

EXAMPLE I The Best Mode

We make the following mix:

Material:	Parts by weight
Boron carbide of Table I, B _{4.3} C-----	50.00
Epoxy resin monomer, Araldite 502-----	8.50
Hardener, Bondmaster CH-44-----	.90
Para dichloro benzene, #400 rice (rice is a known term and #400 averages 60 mesh size) -----	39.20
Toluol -----	1.40
	100.00

The PDB is broken up to see that all the grains are separated. The epoxy resin monomer is mixed with the hardener and stirred for about a minute. Then the toluol is added to the epoxy monomer and the hardener and further mixed for about a minute. We then add to this liquid the boron carbide which is preferably heated to about 150° F. This is not critical and room temperature boron carbide can be used. We now mix this moist sandy mix in a Hobart mixer, or any other mixer can be used, for a period of about two minutes and scrape down the pan. These mixing times are good for batches of almost any practical size. Our largest batches have been thirty-two pounds, with many that were smaller down to fifteen pounds and much larger batches than thirty-two pounds could be mixed in the manner indicated. Then we add the PDB, mix for one-half minute, scrape and mix again for forty-five seconds. This of course can be varied. The mix is now made up.

The shapes ordered are various. We cannot give these shapes because they are classified. Suffice it to say that almost any reasonable shape can be made using known molding technique. However, it can be said that the insides of the mold have been coated with Teflon, which is an anti-sticking agent. Teflon is polymerized tetra fluoro ethylene. Any polymerized fluorinated hydrocarbon having from two to five carbon atoms inclusive, e.g. tri fluoro chloro ethylene, can be used. Mixtures can be used. In certain cases we have lined the molds with glass fiber coated with Teflon. In every case it is the polymer which is the coating. The coating is sprayed in place on steel or graphite molds and then cured at about 700° F.

The mix is now put into the mold in batches. The number of batches will depend on the height of the mold. We have charged the batches to depths of anywhere from 3½ to 7½". Each batch is carefully levelled and then weighted on top and then vibrated. The vibrating is done on a vibrating table with a frequency on the order of 1000 cycles. We have used a Syntron vibrating table. The vibrations are vertical and the amplitude can be changed. After a layer has been vibrated in place, it is roughened on the surface and then another layer is added. This goes on until the mold is filled.

A final pressing is performed pneumatically with a top mold plate with a pressure of the order of ten pounds per square inch. The stated figures give an example of the best mode and these details can be widely varied.

Now the pressed mixture is allowed to stay in the mold for twenty-four hours or this can be varied. The mix starts to set and at the end of twenty-four hours the green piece can be removed, the mold being taken apart. Then the green piece out of the mold is put on a rack in front of an exhaust system and allowed to stand for another day at room temperature. Then the green piece which is now mostly cured is put in an oven and heated to a temperature of 185° F. for two to three days, best example three days, and this drives out the PDB or other volatile agent. The PDB melts and flows out, but whatever is trapped in the pores eventually volatilizes leaving no residue.

The foregoing completes a neutron shield in some cases but in other cases it is machined or ground to exact shape. The specific gravity of a shield made in accordance with the foregoing description is .84 which of course will vary slightly from time to time from about .83 to .85. This gives .54 gram per cubic centimeter of boron in the shield which is what is desired, that is not less than .54 gram per cubic centimeter with a specific gravity of less than 1.0. This was the specification to be met presented to us and by our invention we have more than met the specification. The specific gravities mentioned herein are always bulk specific gravities on account of the pores in many of the shields. We cannot predict the lowest specific gravity which we can achieve but this is set by the compressive strength which should be at least 100 pounds per square inch, and these limits are therefore complementary.

EXAMPLE II

For the manufacture of a shield with .54 gram per cubic centimeter and a specific gravity of .76, we proceed exactly as described above using, however, the mix of Table III.

Material:	Parts by weight
Boron carbide of Table I, B _{4.3} C-----	50.00
Epoxy resin monomer, Araldite 502-----	5.07
Hardener, Bondmaster CH-44-----	.53
Para dichloro benzene, #400 rice (rice is a known term and #400 averages 60 mesh size) -----	42.60
Toluol -----	1.80
	100.00

EXAMPLE III

For the manufacture of a neutron shield having .54

gram per cubic centimeter of boron with a specific gravity of .92, we proceed exactly as above described using, however, the mix of the following table:

TABLE IV

Material:	Parts by weight
Boron carbide of Table I, $B_{4.3}C$ -----	48.50
Epoxy resin monomer, Araldite 502-----	14.10
Hardener, Bondmaster CH-44-----	1.40
Para dichloro benzene, #400 rice (rice is a known term and #400 averages 60 mesh size)-----	36.00
Toluol -----	100.00

EXAMPLE IV

Sometimes a denser shield is wanted. For the manufacture of a shield with a specific gravity of 1.90 we proceed as follows:

TABLE V

Material:	Parts by weight
Boron carbide of Table I, $B_{4.3}C$ -----	80.00
Epoxy resin monomer, Araldite 502-----	18.00
Hardener, Bondmaster CH-44-----	2.00
	100.00

The resin and the hardener were first mixed as described, then the boron carbide was added and further mixed as described. Then this mixture was puddled in a mold lined with Teflon, this mixture being a fairly free-flowing mix. No pressing operation was used and the mix was cured with a top cover for twenty-four hours and then without a cover for twenty-four hours more, all at room temperature. The mold was then stripped and the neutron shield was complete. This shield had a density of boron of 1.2 grams per cubic centimeter.

We can achieve a large range of light weight shields and boron content by varying the proportions of boron carbide, epoxy resin and volatile organic solids. A range of from .05 to 1.3 grams per cubic centimeter of boron is readily obtainable. By varying the specifications, the physical properties such as compressive strength and impact resistance can also be varied. The shield of Example I had a compressive strength of from 300 to 500 pounds per square inch, of Example II from 150 to 300 pounds per square inch, of Example III from 500 to 800 pounds per square inch, of Example IV from 1500 to 3000 pounds per square inch. The reason for the wide range is because it depends where you take the cross section; at the skin the compressive strength is greater.

The advantages of using boron carbide and epoxy resin for neutron shields have in part been pointed out and will now be further explained, sometimes by way of pointing out undesired characteristics of other components. Boron carbide in an inexpensive material having a high neutron capture cross section. It is otherwise inert and solid at all temperatures and atmospheres contemplated. It doesn't react with the epoxy resin but it is well bonded thereby. The epoxy resin cures at room temperature and the components can be stored (the monomer and the hardener) indefinitely until mixed. Polyethylene has to be hot pressed and with it shields would be difficult to fabricate. Epoxy resin is little subject to decay due to neutron bombardment, while many resins such as phenolic resin are not and also require heat to set.

The best volatile agents of which we had any knowledge are PDB and naphthalene. Naphthalene used to be used in industry until PDB was found to be better. It is almost universally used today for a pore forming volatile agent as it leaves no residue and neither does naphthalene. The latter is entirely practical.

The melting point of PDB is 127.2° F. and its boiling point is 345.0° F., assuming atmospheric pressure of 760 millimeters of mercury. The melting point of naphthalene is 176° F. and its boiling point is 424.4° F. at 760 milli-

meters. The vapor pressure of PDB at various temperatures is shown in the following table.

TABLE VI

Vapor Pressure of PDB

Temperature, ° F.:	Pressure mm. of mercury
130.6 -----	10
184.6 -----	40
227.1 -----	100
302.4 -----	400
345.0 -----	760

Any other volatile agent leaving no residue could be used which has a vapor pressure of at least 20 millimeters of mercury at 185° F. Baking can be from 127° F. to 345° F.

Since bisphenol A monomer and bisphenol F monomer are quite compatible and can be mixed and so are their diglyceride ethers and the mixtures will make good resins, we wish to claim the mixtures. Also mixtures of PDB and naphthalene can be used.

In Example I the percentage of boron carbide by weight of the shield is about 84%. In Example II the percentage of boron carbide by weight of the shield is very nearly 90%. In Example III the percentage of boron carbide by weight of the shield is 75.7%. This can be varied considerably. A little bit more than 90% of boron carbide can be achieved, up to 95%, by using coarse boron carbide. On the other end of the scale there is no limit and useful shields can have very little in some cases as little as 5% of boron carbide.

In order to make a shield with 1.3 grams per cc. of boron using boron carbide having 79.5% of boron, the specific gravity of the shield would be 1.9 if we follow Example IV using 20% of resin. We can achieve specific gravities all the way from .5 to about 2.

It will thus be seen that there has been provided by this invention neutron shields and methods of making them in accordance with which the various objects hereinabove set forth together with many thoroughly practical advantages are successfully achieved. As many possible embodiments may be made of the above invention and as many changes might be made in the embodiments above set forth, it is to be understood that all matter hereinbefore set forth is to be interpreted as illustrative and not in a limiting sense.

We claim:

1. A pressure molded and shaped neutron shield in solid form adapted to be machined consisting essentially of from 5% to 95% by weight of particles of boron carbide dispersed in a cured epoxy resin, said boron carbide particles being sized to be no larger than 20 mesh, and said particulate boron carbide being present in a distribution of variously sized particles.

2. A pressure molded and shaped neutron shield in solid form adapted to be machined consisting essentially of from 5% to 95% by weight of particles of boron carbide dispersed in a cured epoxy resin, said boron carbide particles being sized such that 35% by weight falls within a range of 46 to 66 mesh, 45% falls within a range of 66 to 12 mesh, and 20% falls within a range of 120 to 325 mesh.

3. A pressure molded and shaped neutron shield having a specific gravity of between .5 to 2 consisting essentially of particles of boron carbide held dispersed in a cured epoxy resin of controlled porosity, said boron carbide being present in a range of from 5% to 95% by weight, said epoxy resin forming less than 18% by weight of the shield, and said boron carbide particles being smaller than 20 mesh and consisting of less than 20% screening fines.

4. A raw batch for making a porous pressure molded neutron shield in solid form consisting essentially of a mixture including particles of boron carbide dispersed in an uncured epoxy resin, said mixture also consisting of

particles of a volatile organic solid selected from the group consisting of paradichlorobenzene and naphthalene, said batch being adapted for use with a hardener for said resin.

5. A raw batch for making a porous pressure molded neutron shield in solid form consisting essentially of a mixture including particles of boron carbide dispersed in an uncured epoxy resin, said mixture also consisting of particles of a volatile organic solid selected from the group consisting of paradichlorobenzene and naphthalene, a relatively small proportion of a toluol extender, said batch being adapted for use with a hardener for said resin.

6. A raw batch for making a porous pressure molded neutron shield in solid form consisting essentially of a mixture including particles of boron carbide dispersed in an uncured epoxy resin, said mixture also consisting of particles of a volatile organic solid selected from the group consisting of paradichlorobenzene and naphthalene, an extender selected from the group consisting of toluol, methyl ethyl ketone, ethyl ethyl ketone, acetone and mix-

tures thereof, said batch being adapted for use with a hardener for said resin.

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