COMMONWEALTH OF AUSTRALIA
PATENTS ACT 1952-1966

APPLICATION FOR A PATENT

COMPLETE AFTER PROVISIONAL SPECIFICATION No. 18686/83

CHEMLINE PTY. LTD.

of 50 Cavan Road, Dry Creek,
State of South Australia,
Commonwealth of Australia

hereby apply for the grant of a Patent for an invention entitled
"LINING POLYMERS WITH ELASTOMERS"

which is described in the accompanying provisional\complete specification.

Our address for service is care of R. K. MADDERN & ASSOCIATES, Patent Attorneys, 97 King William Street, Adelaide, South Australia.

Dated this 13th day of September 1982.

CHEMLINE PTY. LTD.,

By its Patent Attorneys,
R.K. MADDERN & ASSOCIATES.

TO:
THE COMMISSIONER OF PATENTS,
CANBERRA, A.C.T.
DECLARATION IN SUPPORT OF AN APPLICATION FOR A PATENT OR PATENT OF ADDITION

In support of the Application
made by CHEMLINE PTY. LTD.

for a patent/patent-of-addition for an invention entitled
"LINING POLYMERS WITH ELASTOMERS"

Full name(s) of declarant(s).
I/we. MALCOLM DOUGLAS CAMPBELL

Address(es) of declarant(s).
of 50 Cavan Road, Dry Creek, State of South Australia,
Commonwealth of Australia

do solemnly and sincerely declare as follows:

1. I am/We are the applicant(s) for the patent/patent-of-addition
(or, in the case of an application by a body corporate) to make this declaration on its/their behalf.

2. I am/We are the actual inventor(s) of the invention (or, where a person other than the inventor is the applicant)

Full name(s) of actual inventor(s).
MALCOLM DOUGLAS CAMPBELL and WAYNE GEOFFREY MURPHY

Address(es) of actual inventor(s).
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By virtue of the provisions of Section 34(1)(fa) of the Patents Act 1952-1979

Declared at Dry Creek this 10th day of September, 1982.

Signature(s) of declarant(s).

(Note: No attestation or other signature is required.)

This invention relates to lining or coating of a
LINING POLYMERS WITH ELASTOMERS
CHEMLINE PTY. LTD.
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MALCOLM DOUGLAS CAMPBELL AND WAYNE GEOFFREY MURPHY
MA
Claim
1. An abrasion resistant composite comprising,
an abrasion resistant layer of elastomeric material
having a low modulus of elasticity capable of absorbing
kinetic energy of particles when impinged there-against,
through elastic deformation,
a structural layer of a thermo-setting resin poly-
meric material having a high modulus of elasticity and
a hardness value which is higher than the hardness of the
elastomeric layer, and
a transition layer separating said abrasion resistant
and said structural layers being made of a curable/hardenable
mixture of a thermo-setting polymeric resin and an elasto-
meric resin and having modulus of elasticity and hardness
values intermediate those of the elastomeric and polymeric
layers, whereby the transition zone serves to increase the
chemical compatibility between the layers of polymeric and
elastomeric resins and to reduce the likelihood of stresses due to shrinkage being introduced during curing, thermal expansion and of local stress concentrations being introduced due to the impingement of particles onto the elastomeric layer.

14. A composite pipe having an outer layer made from a fibre reinforced thermo-setting synthetic resin, an inner lining made of a polyurethane resin, and an intermediate transition layer between the outer layer and the inner lining, said transition layer comprising a blend of said thermo-setting synthetic resin and said polyurethane resin.

15. A method of making a composite article comprising the steps of applying to a mould or mandrel polyurethane so as to form an abrasion resistant layer, applying to the abrasion resistant layer a mixture of polyurethane and a thermo-setting polymer resin to thereby form a transition layer, applying fibre reinforced resin to the transition layer, demoulding the composite so formed and post-curing.
resins of which the polymeric structural layer and the elastomeric abrasion resistant layer are made.
This invention relates to lining or coating of a polymer or fibre reinforced polymer with an elastomer, more particularly to a composite product thus formed. The invention has special application in the production of slurry pipes used to transport abrasive materials.

It is common practice to line slurry pipes of metal, e.g. steel, or polymeric material, e.g. fibreglass reinforced polyester or epoxy, with an elastomer such as a natural rubber, and more recently, a polyurethane, the lining being effective to absorb the kinetic energy of the particles through elastic deformation thereof. Polyurethane elastomers exhibit excellent corrosion and abrasion resistance which make them particularly suitable for the lining of pipes, for example, where the pipes are used for the passage of abrasive materials. Tests carried out clearly demonstrate that polyurethanes have a significant wear advantage over many other materials, e.g. linatex-rubber, hard neoprene rubber.

There has remained however a hitherto unresolved problem. In the case of a steel or fibreglass reinforced plastics pipe the modulus of elasticity of the pipe wall is likely to be somewhere between 5 and 210 Gpa. The polyurethane or other elastomer however has an elastic modulus between 2 and 50 Mpa and a durometer hardness of

7. A composite according to claim 5 wherein said synthetic resin polymeric material is a polyester, epoxy,
less than 70 shore D and consequently, when the polyurethane is subjected to a force, for example due to impact by a solid object, or fluid flow through a pipe or over a surface, there is a strain incompatibility at the interface between the polyurethane and the polymer. This has very serious practical implications, since it is possible as a result of the stresses generated at the interface, for the polyurethane to debond from the polymer substrate resulting in an acceleration of the rate of wear, and if the polyurethane gets torn the lumps of polyurethane can cause blockages downstream of the location, and in any case, the abrasion and chemical protection afforded by the polyurethane is lost.

Another problem which has hitherto remained unresolved is that upon setting, there is a different shrinkage rate between the urethane and the polymeric substrate which can result in the interface being a highly strained weakened zone, and in turn result in the polyurethane debonding from the substrate. A still further problem which is sometimes encountered is that local debonding in the form of bubbles can develop at the interface when the polyurethane is in contact with water because of the osmotic pressure of water which permeates the polyurethane and collects at the interface. From the foregoing, it will be thus appreciated that in composite or laminated articles, an interface between

14. A composite pipe having an outer layer made from a fibre reinforced thermo-setting synthetic resin, an inner lining made of a polyurethane resin, and an intermediate...
layers of dissimilar materials can be source of weakness
due to the marked physical and chemical property differences
between the materials.

With the object of overcoming the abovementioned
problems, broadly according to this invention, there is
provided a composite comprising a polymeric structural
layer, an abrasion resistant elastomeric layer, and a
transition layer or zone between the structural layer and
the abrasion resistant layer made of a mixture of a poly-
meric resin and an elastomeric resin.

More specifically, according to this invention a com-
posite comprises an abrasion resistant layer of elastomeric
material having a low modulus of elasticity capable of
absorbing kinetic energy of particles when impinged there-
against, through elastic deformation, a structural layer
of a thermo-setting resin polymeric material having a high
modulus of elasticity and a hardness value which is higher
than the hardness of the elastomeric layer, and a transition
layer separating said abrasion resistant and said structural
layers being made of a curable/hardenable mixture of a
thermo-setting polymeric resin and an elastomeric resin and
having modulus of elasticity and hardness values intermediate
those of the elastomeric and polymeric layers, whereby the
transition zone serves to increase the chemical compatibility
between the layers of polymeric and elastomeric resins and

and said transition layers are modified by the addition
of fillers and/or fibrous reinforcement.
to reduce the likelihood of stresses due to shrinkage being introduced during curing, thermal expansion and of local stress concentrations being introduced due to the impingement of particles onto the elastomeric layer.

Preferably, the polymeric material is formed of a thermo-setting polymer having generally visco-elastic properties and may be selected from the group consisting of polyester, epoxy, vinylester and bisphenolic resins; whilst the elastomer is formed of a thermo-setting or thermoplastic elastomeric resin having sigmoidal stress/strain curve characteristics such as a polyurethane elastomer.

Ideally, the composite article of this invention consists of a polymeric substrate, an abrasion resistant elastomeric layer, and an intermediate transition polymeric/elastomeric layer, the composition of which progressively changes from 100% elastomer (nearest the elastomer layer) to 100% polymer. In practice, such an ideal composite article can be manufactured by applying the elastomeric resin to a mould, then blending in successively increasing amounts of the polymeric resin whilst decreasing the amount of the elastomeric resin until 100% polymer is achieved, for example by dual spray application.

From a practical viewpoint, it has been found that a satisfactory composite can be manufactured by using a uniform blend of resins for the transition layer or zone.
That is, one applies the elastomer to the mould followed by the application of a single composition transition layer, e.g. a blend of 25% (by weight) polymer, 75% (by weight) elastomer, after which a 100% polymer layer is applied.

The process need not be continuous, however, a continuous operation is considered ideal.

The composition of the transition layer or zone may incorporate additional ingredients, amongst which includes filler agents (e.g. clay, calcium carbonate, etc.) and reinforcement materials (e.g. glass fibre, nylon fibre, etc.). The function of the filler or reinforcement is to tailor the elastic properties of the transition zone to further increase the compatibility (both physical and chemical) between the polyurethane liner and the structural fibre reinforced polymer layer. The elastomer layer may also be reinforced to improve cut resistance, so too may the structural polymer layer be reinforced.

This invention thus provides a composite having a transition region between the dissimilar materials which is compatible to both of these materials, the transition layer normally being composed of a physical mix of components which are the same as the other materials. The presence of the transition zone is effective to greatly reduce stress concentration due to the absence of interfaces and progressively decrease the permeability of the material to osmotic water.
flow. With this invention, there is no single continuous interface where debonding can occur.

The invention is applicable to many if not most products wherein an elastomeric lining or coating is required over the surface of a polymer and its greatest usage would be in pipes, tanks, vessels, cone separators and other types of separators for mining purposes, and other mining process equipment.

Listed here below are examples of the most suitable resins for use in the manufacture of a composite according to this invention (all of these resins being well known in the art).

(a) Polyurethane resins commercially available under the trade names of Vibrathane, Vibraspray, Vibrapair (registered trade marks of Uniroyal, Inc.); WRM-80 (Du Pont); Irathane 100, 200 series resins (Irathane International Ltd.); and Baytec (trade mark of Bayer).

(b) Polymeric resins.
   (i) Polyester

   Both Iso and Ortho phthalic polyester resins

   Suitable resins include -

   Monsanto Crystic 272, 161, 545
   A.C. Hatrick Polylite 61-340, 61-345
   Kemrez Cellobond A2784, KEM 210.
(ii) Bisphenolic

Suitable bisphenolic resins include -

Monsanto Crystic 600
A.C. Hatrick Polylite 31-382

(iii) Vinylester

Dow Chemical Derakane 411, 470
A.C. Hatrick Corrolite 61-745

(iv) Epoxy

Epoxy resins of the type

WPE 170
WPE 180

Reinforcements that may be successfully incorporated into the transition zone and/or the polymer include -

Glass fibre in the form of chopped strand mat, continuous rovings, woven rovings or cloth surfacing tissues, etc.

Nylon fibres in the form of non-woven mat; Cerex (trade mark of Monsanto) continuous filaments, scrim cloth, etc.

Nexus (trade mark) fabric
Kevlar (trade mark) fibres
Nomex (trade mark) fibres
Carbon fibres, etc.

Fillers that may be successfully incorporated into the transition zone and/or the polymer include -
Kaolin clay
Mica
Talc
Calcium carbonate, etc.

5. Several examples of this invention are described here-under to further illustrate the present invention but it should be understood that the examples are by way of illustration only and should not be construed as limiting the invention in any way.

10. In the first example, the interior surface of a fibreglass reinforced polyester resin pipe is described as being lined with a polyurethane elastomer.

15. The first stage of the production is to form the inner lining of the pipe and this is achieved by applying a polyurethane resin to a release membrane positioned over the surface of a heated, rotating, forming mandrel. The required thickness is built up by applying successive layers, and when sufficient thickness has been built up for the pipe to be useful for its purpose, a mixture of the same polyurethane and the polyester resin is applied to the outer surface of the laid up lining to thereby form the transition layer. Application may be by any one of several well known means including immersion in a trough, in-line mixing, or mixing two streams as they emerge from respective discharge spouts, but in this example, the
resins are mixed in the a:r by spraying each independently into the other and the mixture onto the surface of the uncured laid up polyurethane.

At this stage in the process, filler agents and/or reinforcement materials are introduced. Fillers may be added to the transition zone by mixing the desired amount into the polymer resin component. Reinforcement may be added by spraying chopped strands (e.g. from a Venus Glass Chopper gun) or spirally winding a ribbon or tape of reinforcement into the transition zone.

Although use can be made of a solvent type polyurethane, this is found to be much less suitable than a plural component solvent-less polyurethane such as those sold under the trade names "Vibraspray 80" or "Baytec".

Most desirably, there should be a blend over a full range across the thickness of the blend layer, such that the proportion of the polymer resin gradually increases from 0% to 100% (by weight) while the proportion of the elastomer resin decreases from 100% to 0% (by weight).

However in practice it is not always necessary to have such a smooth transition across the thickness of the layer and instead one may have the transition layer composed of a mere admixture of the two resins.

After the transition blend layer has been applied, a fibreglass reinforced synthetic resin is applied in accordance
with known art, for example by filament winding of rovings while applying a resin to the rovings or by hand lay up. The component is then post-cured at an elevated temperature. Although the above example has been limited to a pipe which is formed by layer method, it will be clear the invention is not so limited. For example the pipe could first be formed by known prior art methods (e.g. centrifugal casting) and the blend layer could be applied within the pipe from a travelling spray or discharge head, and subsequently the layer of polyurethane could be applied, all the while rotating the pipe to ensure an even thickness.

The second example relates to the manufacture of a cone deck separator used in the gravity separation of minerals. A female mould is rotated and solvent-less polyurethane is sprayed until the desired thickness is achieved, then a resin spray is admixed with the polyurethane spray with the polyurethane component being decreased as the resin component is increased until a 100% resin is achieved, then chopped glass from a chopper gun is admixed with the resin stream. This continues until the thickness of the fibre reinforced resin reaches the required level. The component is then trimmed, removed from mould and post cured.

Although the tests so far carried out by the Applicant have made use of polyurethane elastomers and thermo-setting polymers, it will be art that any other wherein the elastomers and achieve the can be used.
polymers, it will be appreciated by those skilled in the art that any other polymeric/elastomeric resin combination wherein the elastomer and polymer can cure/harden independently and achieve their mechanical properties when intimately mixed can be used.
The claims defining the invention are as follows:

1. An abrasion resistant composite comprising,
    an abrasion resistant layer of elastomeric material
    having a low modulus of elasticity capable of absorbing
    kinetic energy of particles when impinged there-against,
    through elastic deformation,
    a structural layer of a thermo-setting resin poly-
    meric material having a high modulus of elasticity and
    a hardness value which is higher than the hardness of the
    elastomeric layer, and
    a transition layer separating said abrasion resistant
    and said structural layers being made of a curable/hardenable
    mixture of a thermo-setting polymeric resin and an elasto-
    meric resin and having modulus of elasticity and hardness
    values intermediate those of the elastomeric and polymeric
    layers, whereby the transition zone serves to increase the
    chemical compatibility between the layers of polymeric and
    elastomeric resins and to reduce the likelihood of stresses
    due to shrinkage being introduced during curing, thermal
    expansion and of local stress concentrations being introduced
    due to the impingement of particles onto the elastomeric
    layer.

2. A composite according to claim 1 wherein said
    polymeric and said elastomeric resins or which said
    transition layer is made are respectively the same as the
resins of which the polymeric structural layer and the elastomeric abrasion resistant layer are made.

3. A composite according to either claim 1 or claim 2 wherein said transition layer comprises a blend of said polymeric and elastomeric resins, the composition of the blend being uniform throughout the thickness of said transition layer.

4. A composite according to either claim 1 or claim 2 wherein said transition layer comprises a blend of said polymeric and elastomeric resins, the composition of the blend being made so that the proportion (by weight) of the elastomeric resin decreases, from the abrasion resistant layer to the structural layer, across the thickness of the transition layer whilst correspondingly the proportion (by weight) of the polymeric resin increases.

5. A composite according to any preceding claim wherein said resin polymeric material is a thermo-setting synthetic polymer having generally visco-elastic properties.

6. A composite according to any preceding claim wherein said elastomeric material is a thermo-setting or thermoplastic polymer having sigmoidal stress/strain curve characteristics.
7. A composite according to claim 5 wherein said synthetic resin polymeric material is a polyester, epoxy, vinylester or bisphenolic resin.

8. A composite according to claim 5 wherein said elastomeric material is polyurethane.

9. A composite according to claim 1 wherein said structural layer is made of a polymeric resin selected from polyester, epoxy, vinylester and bisphenolic resins, said abrasion resistant layer is made of a polyurethane resin, and said transition layer is made from a blend of a selected one of said polymeric resins and said polyurethane resin.

10. A composite according to claim 1 or claim 2 wherein said polymeric layer is made of a synthetic resin reinforced with fibres made of glass, nylon, carbon or Kevlar.

11. A composite according to any preceding claim wherein said abrasion resistant layer is fibre reinforced.

12. A composite according to any preceding claim wherein said transition layer is fibre reinforced.

13. A composite according to any preceding claim wherein the composition of said transition layer comprises filler agents.
14. A composite pipe having an outer layer made from a fibre reinforced thermo-setting synthetic resin, an inner lining made of a polyurethane resin, and an intermediate transition layer between the outer layer and the inner lining, said transition layer comprising a blend of said thermo-setting synthetic resin and said polyurethane resin.

15. A method of making a composite article comprising the steps of applying to a mould or mandrel polyurethane so as to form an abrasion resistant layer, applying to the abrasion resistant layer a mixture of polyurethane and a thermo-setting polymer resin to thereby form a transition layer, applying fibre reinforced resin to the transition layer, demoulding the composite so formed and post-curing.

16. A method of making a composite article comprising the steps of forming a fibre reinforced thermo-setting synthetic resin substrate on a mould or mandrel; applying onto the substrate a mixture of a polyurethane and thermo-setting polymeric resin so as to form a transition layer; applying a polyurethane onto the transition layer so as to form an abrasion resistant layer; demoulding the composite article thus formed and post-curing.

17. A method of making a composite article according to either claim 15 or claim 16 wherein said polyurethane
and said transition layers are modified by the addition of fillers and/or fibrous reinforcement.

18. A method of making a composite article according to either claim 15 or claim 16 wherein said polyurethane and said transition layers are applied by a spraying technique.

19. A composite produced substantially in accordance with the description contained herein.

20. A pipe manufactured substantially in accordance with the example described herein.

DATED this 2nd day of September 1983.

CHEMLINE PTY. LTD.

By its Patent Attorneys,

R.K. MADDERN & ASSOCIATES.