

PATENT SPECIFICATION

(11) 1383 422

1383 422

- (21) Application No. 24663/72 (22) Filed 25 May 1972
 (61) Patent of Addition to No. 1087566 dated 1 Feb. 1966
 (23) Complete Specification filed 15 May 1973
 (44) Complete Specification published 12 Feb. 1975
 (51) INT CL² A63B 37/12
 (52) Index at acceptance

A6D 1A 1C2 1C3 1C4
 C3P 4C13B 4C8B 4D3B1 4D8 4K7 4K8 7C13B 7C8B
 7D1A 7D8 7K4 7K8 7T2A 7T2D 8C13B 8C8B
 8D1A 8D1B 8D2A 8D2B2 8D8 8K7 8K8 8T2A
 8T2D F

(72) Inventors JOHN VINCENT BENNETT and
 STANLEY RICHARD HARRISON



(54) IMPROVEMENTS IN GOLF BALLS

(71) We, DUNLOP LIMITED, a British Company of Dunlop House, Ryder Street, St. James's, London SW1Y 6PX, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to golf balls and in particular to golf balls having a construction in the form of a central core surrounded by a separately-formed cover.

The invention provides a golf ball comprising a thread-wound core and a cover for said core, said cover being formed of a blend of two copolymers, the first copolymer being of a mono-olefine and an unsaturated carboxylic acid and the second copolymer being of ethylene and vinyl acetate.

The ethylene-vinyl acetate copolymer (hereafter referred to as E.V.A.) is suitably present in the blend in an amount of from 5% to 30% by weight of the total first and second copolymers. The E.V.A. copolymer preferably contains from 10% to 40% by weight of vinyl acetate.

The mono-olefine-unsaturated carboxylic acid copolymer, i.e. the first copolymer, is conveniently formed from ethylene and a mono-basic or di-basic carboxylic acid. Methacrylic acid and acrylic acid are the preferred unsaturated acids. The first copolymer may, if desired, contain small amounts, e.g. less than 10% by weight of other monomers. Suitable other monomers include vinyl alkanolic esters, alkyl acrylates and alkyl methacrylates.

The first copolymer conveniently contains a number of thermolabile cross-linkages to increase the hardness, resilience, toughness and stiffness of the solid mixture so produced. This can be achieved by employing a terpolymer with a metal salt of the acid. For example metal having a valency of from 1 to 4 e.g.

sodium or zinc salts, can be used. A typical polymer is a terpolymer of ethylene, methacrylic acid and sodium methacrylate. Alternatively, thermolabile cross-linkages can be introduced into the composition immediately prior to its use for the manufacture of the cover of the golf ball or can preferably be introduced sometimes previously, e.g. a metal salt can be reacted with the first copolymer at elevated temperatures such that the volatiles are removed prior to use of the copolymer composition for the manufacture of the cover. The composition containing the thermolabile cross-linkages remains thermoplastic, although the viscosity of the molten composition is greater than that of a composition which does not contain the thermolabile cross-linkages. The cross-linked composition has increased hardness and toughness in comparison with non-cross-linked compositions.

The additive used to introduce the thermolabile cross-linkages into the first copolymer is an inorganic or organic metal compound whose metal forms ionic associations with the carboxyl groups in the polymer and typical metal compounds are the acetates, alkoxides, oxides, carbonates and hydroxides. Preferably mono- or divalent metal compounds are used, and examples of suitable compounds are the acetates of sodium and potassium or the oxides of calcium, magnesium and zinc. Compounds of trivalent and tetravalent metal such as aluminium or lead may also be used.

The amount of additive that is mixed with the copolymer is preferably less than that theoretically required to react with all the acid groups in the copolymer and usually is not more than 85% of the stoichiometric equivalent of the total unsaturated carboxylic acid. Preferably, 10% to 75% and especially 15% to 60% of the stoichiometric equivalent of the carboxylic acid is used.

The first copolymer preferably contains no

[Price 33p]

Price 75p

more than 30% by weight of the unsaturated carboxylic acid, although higher percentages may be used, and the first copolymer especially contains no more than 20% by weight of the unsaturated acid. If a metal salt of an acid is used, the metal is similarly preferably present in an amount of not more than 85%, preferably from 10% to 75%, and especially 15% to 60% of the stoichiometric equivalent of the carboxylic acid. The copolymers are thermolabile and have a lower softening point than homopolymers of the olefine.

The composition used to form the cover of the golf ball can contain a filler which can be an active filler, i.e. one which acts as the additive to provide thermolabile cross-linkages as well as the filler. In the case where an active filler is used there is then generally no need for an additional additive to be employed, since a proportion of the filler acts in this way. Examples of active fillers are zinc oxide and magnesium oxide. The incorporation of a filler improves the properties of the composition, particularly in regard to the cutting-resistance, which is exceedingly important in connection with golf balls. The amount of filler that is fixed with the copolymer may be up to 20% by weight of the combined first and second copolymers.

As indicated above, the invention is particularly concerned to provide a golf ball having a conventional, thread-wound core. A core of this type has a centre which can be either solid or a small spherical sac filled with a liquid or paste and has wound on the centre a layer of rubber thread or tape. The cover which is to surround this core must then of

course give adequate protection to the fragile thread-windings but at the same time it should not detract from the resilience and flight properties desired in the finished ball. Moreover, in order to be acceptable to golfers the cover must provide the ball with acceptable "click". The "click" of a golf ball is the noise which the ball makes when it is struck by the club and is an extremely important property to golfers. Balls of the invention have been found to have extremely acceptable "click" whilst retaining the excellent flight properties and resilience that are demanded by serious golfers.

The invention is further described in the following Examples.

EXAMPLES 1 TO 6

In these Examples a number of golf ball cover compositions were made up from blends according to the invention and were formed into slabs and tested for various physical properties. The various blends were then formed into golf ball cover half-shells and were moulded around conventional, thread-wound golf ball centres by conventional means. The balls so formed were tested for flight properties and "click".

EXAMPLES 7 AND 8

Similar tests were carried out on a conventional cover material and on a material based on the first copolymer defined above alone.

The blends used in the Examples and the results obtained are listed below in Tables 1 and 2 respectively.

TABLE 1

Example No.	Copolymer A	Copolymer B	Copolymer C	Copolymer D
1	95	5	—	—
2	90	10	—	—
3	85	15	—	—
4	80	20	—	—
5	90	—	10	—
6	90	—	—	10
7	100	—	—	—
8*	—	—	—	—

*Example 8 was a conventional cover material based on a *trans*-polyisoprene/balata mix. Copolymer A—copolymer of ethylene and methacrylic acid containing 14% by weight of acid of which 54% is in the form of the sodium salt.

Copolymer B—copolymer of ethylene and vinyl acetate containing 28% by weight of vinyl acetate.

Copolymer C—as for copolymer B with 18% by weight vinyl acetate.

Copolymer D—as for copolymer B with 40% by weight vinyl acetate.

TABLE 2

(a) Slab Properties

Example No.	Hardness (Shore D)	Tear-Resistance (Kg/tp)	Cutting Index
5	1 65	32	405
	2 63.5	29	405
	3 61.5	27	395
	4 60	24	385
	5 64.5	29	405
10	6 61.5	26	385
	7 67	32	415
	8 62	19	320

(b) Ball Properties

Example No.	Carry	Total Flight	Trajectory	"Click"
15	1 228	263	30	sharp
	2 227	264	30	good
	3 226	262	30	good
	4 224	260	29	good
	5 227	263	30	sharp
20	6 225	260	29	good
	7 227	265	30	very sharp
	8 228	261	31	good

The flight properties of all the balls tested were very similar but the sound made on impact between the club depends on the type and amount of the ethylene vinyl acetate copolymer used and can be estimated to some degree by hardness measurements taken on a slab of the cover material. It will be seen from the above results that balls having covers made according to the present invention, i.e. based on a blend of two copolymers, had more acceptable "click" than a ball whose cover was made from the first copolymer alone.

Cutting-resistance and tear-resistance of all the blends considered was better than for the standard material but decreased, as expected, with increasing amount of vinyl acetate. For maximum cut-resistance and flight performance (resilience), the smallest amount of ethylene-vinyl acetate copolymer which gives the desirable "click" is thus preferred for optimum properties.

45 WHAT WE CLAIM IS:—

1. A golf ball comprising a thread-wound core and a cover for the core, the cover being formed of a blend of two copolymers, the first copolymer being of a mono-olefine and an unsaturated mono- or dicarboxylic acid and the second copolymer being of ethylene and vinyl acetate.

2. A golf ball according to claim 1, in which the ethylene-vinyl acetate copolymer is present in the blend in an amount of from 5 per cent to 30 per cent by weight of the total first and second copolymers.

3. A golf ball according to claim 1 or 2, in which the ethylene-vinyl acetate copolymer

contains from 10 per cent to 40 per cent by weight of vinyl acetate.

4. A golf ball according to claim 1, 2 or 3, in which the first copolymer is a copolymer of ethylene with the mono-basic or dibasic carboxylic acid.

5. A golf ball according to any one of the preceding claims, in which the unsaturated carboxylic acid of the first copolymer is methacrylic acid or acrylic acid.

6. A golf ball according to any one of the preceding claims, in which the first copolymer contains a vinyl alkanolic ester, an alkyl acrylate or an alkyl methacrylate as an additional monomer constituent.

7. A golf ball according to any one of the preceding claims, in which the first copolymer contains a number of thermolabile cross-linkages.

8. A golf ball according to claim 7, in which the thermolabile cross-linkages are obtained by forming the first copolymer as a terpolymer of the olefine, the unsaturated carboxylic acid and a metal salt of the unsaturated carboxylic acid.

9. A golf ball according to claim 8, in which the metal is present in an amount of up to 85 percent of the stoichiometric equivalent of the total unsaturated carboxylic acid.

10. A golf ball according to claim 8 or 9 in which the metal is present in an amount of from 10 per cent to 75 percent of the stoichiometric equivalent of the total unsaturated carboxylic acid.

11. A golf ball according to claim 8, 9 or 10, in which the metal has a valency of from 1 to 4.

TABLE 2

(a) Slab Properties

(c) Gas Properties				
	Example No.	Hardness (Shore D)	Tear-Resistance (Kg/tp)	Cutting Index
5	1	65	32	405
	2	63.5	29	405
	3	61.5	27	395
	4	60	24	385
	5	64.5	29	405
10	6	61.5	26	385
	7	67	32	415
	8	62	19	320

(b) Ball Properties

	Example No.	Carry	Total Flight	Trajectory	"Click"
15	1	228	263	30	sharp
	2	227	264	30	good
	3	226	262	30	good
	4	224	260	29	good
	5	227	263	30	sharp
20	6	225	260	29	good
	7	227	265	30	very sharp
	8	228	261	31	good

The flight properties of all the balls tested were very similar but the sound made on impact between the club depends on the type and amount of the ethylene vinyl acetate copolymer used and can be estimated to some degree by hardness measurements taken on a slab of the cover material. It will be seen from the above results that balls having covers made according to the present invention, i.e. based on a blend of two copolymers, had more acceptable "click" than a ball whose cover was made from the first copolymer alone.

Cutting-resistance and tear-resistance of all the blends considered was better than for the standard material but decreased, as expected, with increasing amount of vinyl acetate. For maximum cut-resistance and flight performance (resilience), the smallest amount of ethylene-vinyl acetate copolymer which gives the desirable "click" is thus preferred for optimum properties.

WHAT WE CLAIM IS:—

1. A golf ball comprising a thread-wound core and a cover for the core, the cover being formed of a blend of two copolymers, the first copolymer being of a mono-olefine and an unsaturated mono- or dicarboxylic acid and the second copolymer being of ethylene and vinyl acetate.

2. A golf ball according to claim 1, in which the ethylene-vinyl acetate copolymer is present in the blend in an amount of from 5 per cent to 30 per cent by weight of the total first and second copolymers.

3. A golf ball according to claim 1 or 2, in which the ethylene-vinyl acetate copolymer

contains from 10 per cent to 40 per cent by weight of vinyl acetate.

4. A golf ball according to claim 1, 2 or 3, in which the first copolymer is a copolymer of ethylene with the mono-basic or di-basic carboxylic acid.

5. A golf ball according to any one of the preceding claims, in which the unsaturated carboxylic acid of the first copolymer is methacrylic acid or acrylic acid.

6. A golf ball according to any one of the preceding claims, in which the first copolymer contains a vinyl alkanoic ester, an alkyl acrylate or an alkyl methacrylate as an additional monomer constituent.

7. A golf ball according to any one of the preceding claims, in which the first copolymer contains a number of thermolabile cross-linkages.

8. A golf ball according to claim 7, in which the thermolabile cross-linkages are obtained by forming the first copolymer as a terpolymer of the olefine, the unsaturated carboxylic acid and a metal salt of the unsaturated carboxylic acid.

9. A golf ball according to claim 8, in which the metal is present in an amount of up to 85 percent of the stoichiometric equivalent of the total unsaturated carboxylic acid.

10. A golf ball according to claim 8 or 9 in which the metal is present in an amount of from 10 per cent to 75 percent of the stoichiometric equivalent of the total unsaturated carboxylic acid.

11. A golf ball according to claim 8, 9 or 10, in which the metal has a valency of from 1 to 4.



12. A golf ball according to any one of claims 8 to 11, in which the metal salt is a sodium or zinc salt.
- 5 13. A golf ball according to any one of claims 8 to 12, in which the first copolymer is a terpolymer of ethylene, methacrylic acid and sodium methacrylate.
- 10 14. A golf ball according to claim 7, in which the thermolabile cross-linkages are obtained by reaction of the first copolymer with an inorganic or organic metal cross-linking agent whose metal forms ionic bonds with the carboxyl groups in the first copolymer.
- 15 15. A golf ball according to claim 14, in which the cross-linking agent is an acetate of sodium or potassium.
- 20 16. A golf ball according to claim 14, in which the cross-linking agent is an oxide of calcium, magnesium or zinc.
17. A golf ball according to claim 14, 15, or 16, in which the amount of the cross-linking agent is up to 85 percent of the stoichiometric equivalent of the carboxylic acid in the first copolymer.
18. A golf ball according to claim 17, in which the amount of the cross-linking agent is from 10 per cent to 75 per cent of the stoichiometric equivalent of the carboxylic acid in the copolymer.
19. A golf ball according to any one of the preceding claims, in which the unsaturated carboxylic acid of the first copolymer is present in an amount up to 30 per cent by weight of the first copolymer.
20. A golf ball according to any one of the preceding claims, in which the cover contains a filler material.
21. A golf ball according to claim 20, in which the filler material is present in an amount of up to 20 per cent by weight of the combined first and second copolymers.
22. A golf ball substantially as hereinbefore described with reference to Examples 1 to 6.
- R. I. G. McKAY,
Agent for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1975.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.



* C L M S *