

IMPROVEMENTS IN OR RELATING TO PLASTICS OVENWARE

THIS INVENTION relates to plastic ovenware.

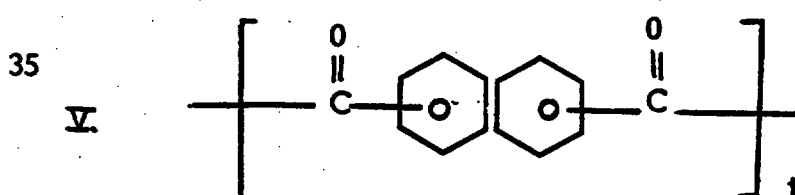
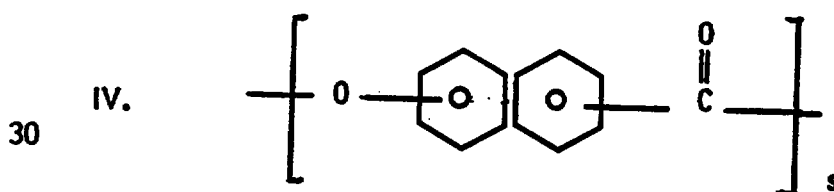
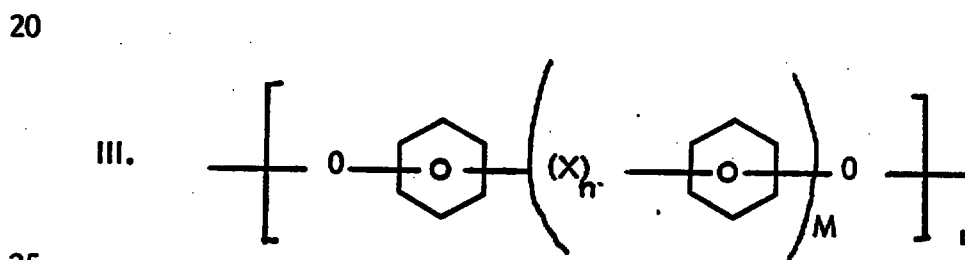
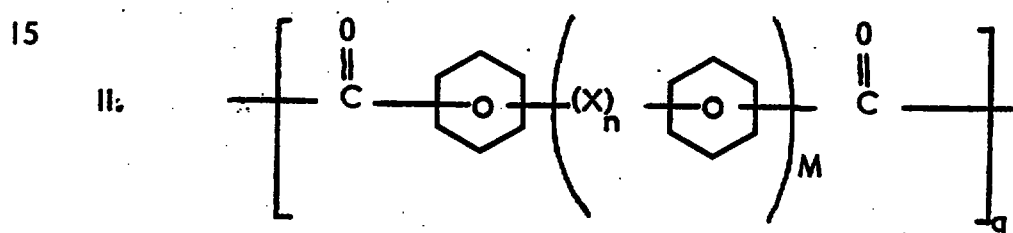
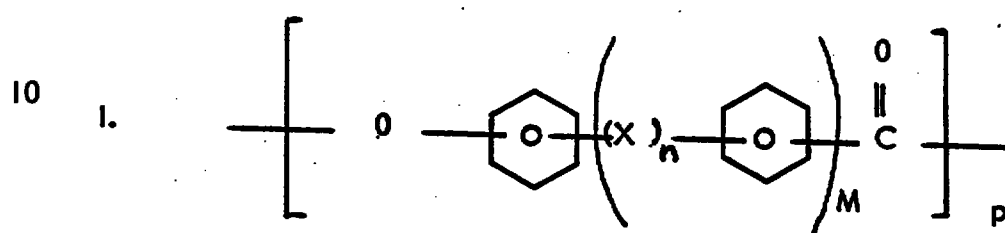
It is known that certain plastics materials have found some application in the ovenware field. For example, polymethylpentene has been used for injection
5 moulded trays which can be used in the preparation of foods. Polysulphone has also been employed in food handling applications. However, no satisfactory material has been found possessing utility over the wide ranges of conditions which are encountered in the provision of
10 cook-in containers, or ovenware, which can be used in either thermal ovens or microwave ovens.

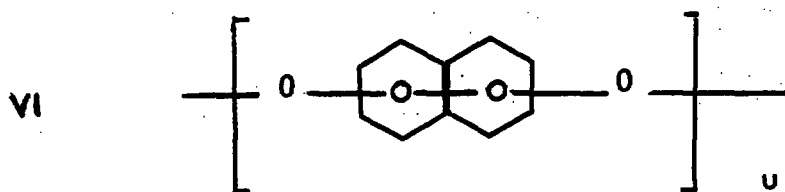
In addition to the necessity for a material which can withstand the temperatures met in the heat source used for cooking, a material must provide a unique combination
15 of a number of other characteristics before ovenware fabricated from the material can be successfully employed in the preparation of food. The material must have good electrical properties. It must be able to undergo severe thermal shocks that is to say, ovenware prepared
20 from it must be capable of going from conditions of extreme cold to high temperatures in relatively brief periods of time. The material must have good hardness and impact strength and possess high tensile and flexural strength. It must also be resistant to boiling water and to adverse
25 effects from immersion in detergents.

The material from which the ovenware is fabricated must be resistant to staining by a wide variety of food-stuffs. It must provide a surface affording good anti-stick properties, and ready releasability for the food
30 which it contains. It must not emit any volatile matter

and it must not have any extractable constituent. And in addition to meeting all of the foregoing requirements, articles prepared from it must present a pleasing appearance.

5 According to this invention there is provided a permanent article of ovenware capable of repeated usage comprising a moulded polyester containing recurrent moieties of one or more of the following formulae:





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where X is, in any given formula, O, S, C = O, NH, or SO₂, n=0 or 1, m = 0 or 1, and the total of the integers p+q+r+s+t+u in the moieties present is from 3 to 800.

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Combinations of the above units include union of a carbonyl group of formula I, II, IV, or V with an oxy group of formula, I, III, IV or VI. In the most general combination units of all the above formulae can be present in a single copolymer. The simplest embodiment would be homopolymers of units I or IV. Other combinations include mixtures of units II and III, II and VI, III and V, V and VI, and I and IV.

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The functional groups are preferably in the para (1,4) positions. They can also be located in the ortho (1,2) position to each other. With respect to the naphthalene moiety, the most desirable locations of the functional groups are 1, 4; 1,5; and 2, 6. The functional groups can alternatively be in the ortho position to each other.

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The symbols p, q, r, s, t and u are integers and indicate the numbers of each unit present in the polymer. The total (p+q+r+s+t+u) can vary from 3-800 and, when present, the ratios q/r; q/u; t/r; t/u; q+t/r+u; and t/r+u can each vary from about 10/11 to about 11/10, with the most preferable ratio being 10/10.

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Examples of materials from which the moieties of formula I may be obtained are p-hydroxybenzoic acid, phenyl-p-hydroxybenzoate, p-acetoxybenzoic acid and isobutyl-p-acetoxybenzoate. Those from which the moieties of formula II are derivable include terephthalic acid, isophthalic acid, diphenyl terephthalate, diethyl isophthalate, methylethyl terephthalate and the isobutyl half ester of terephthalic acid. Among the compounds from which the

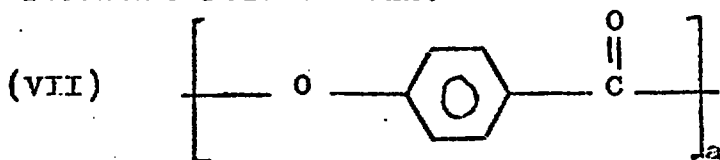
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moieties of Formula III result are p,p'-bisphenol; p,p'-oxybisphenol; 4,4'-dihydroxybenzophenone; resorcinol, and hydroquinone. Inspection will show which of these materials are also suitable for supplying the moieties of Formula VI-VIII, to be described.

Example of monomers represented by Formula IV are 6-hydroxy-1-naphthoic acid, 5-acetoxy-1-naphthoic acid and phenyl 5-hydroxy-1-naphthoate. Monomers representing Formula V include 1,4-naphthalenedicarboxy acid, 1,5-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid and 2,6-naphthalenedicarboxylic acid. The diphenyl esters or dicarbonyl chlorides of these acids can also be used. Examples of monomers representative of Formula VI are 1,4 dihydroxynaphthalene, 2,6-diacetoxynaphthalene, 1,5 and 1,5-dihydroxynaphthalene, and 1,5-dihydroxynaphthalene.

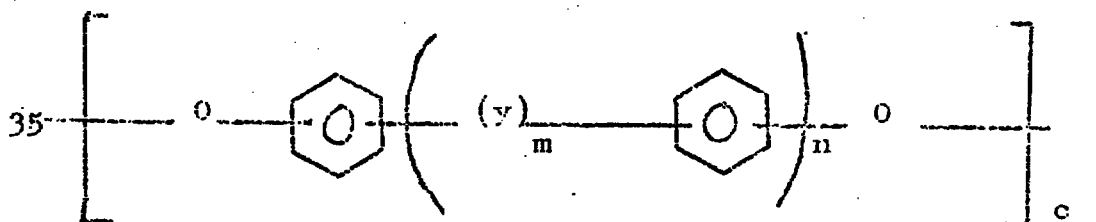
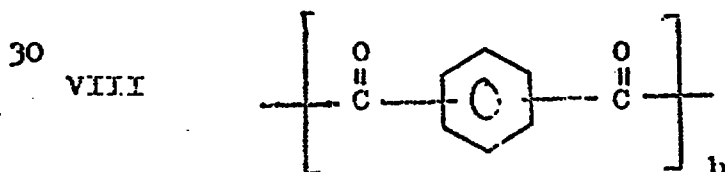
Particularly preferred for use in the practice of the present invention are plastics materials based upon oxybenzoyl polyesters.

The oxybenzoyl polyesters useful in the present invention are generally repeating units of the following formulae Formula VII:



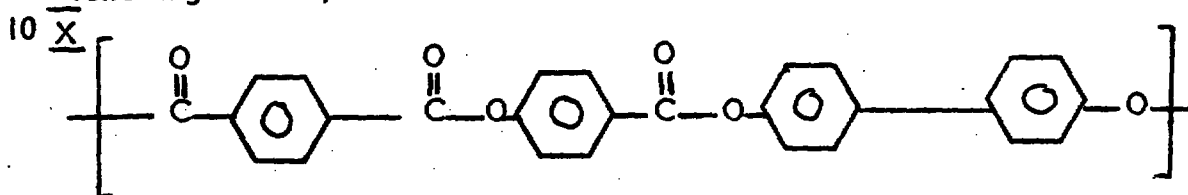
where a is an integer of from about 3 to about 600.

Another preferred class of oxybenzoyl polyesters are copolymers comprising recurring units of Formulae VII, VIII and IX. Formulae VIII and IX are :



wherein y is O or SO₂; m=0 or 1; n=0 or 1; the ratio b:c is between 10:15 and 15:10; the ratio a:b is between 1:100 and 100:1, and a+b+c = 3 to 600, preferably 20 to 200. The carbonyl groups of the moiety of Formula VII or VIII are linked to the oxy groups of a moiety of Formula VII or IX; the oxy groups of the moiety of Formula VII and IX are linked to the carbonyl groups of the moiety of Formula VII or IX.

Preferred copolyesters are those comprising recurring units of the following formula, Formula X.



The synthesis of these polyesters is described in detail in U.S. Patent Application Serial No. 828,484 entitled "P-Oxybenzoyl Copolyesters" the disclosure of which is incorporated herein by reference.

The polyesters useful in the present invention can also be chemically modified by various means such as by inclusion in the polyester of monofunctional reactants such as benzoic acid or tri- or higher functional reactants such as trimesic acid or cyanuric chloride. The benzene rings in these polyesters are preferably unsubstituted but can be substituted with non-interfering substituents, examples of which include among others halogens such as chlorine or bromine, lower alkoxy such as methoxy, and lower alkyl such as methyl.

The oxybenzoyl polyesters useful in the present invention can be employed with various fillers of types and in amounts which do not materially affect the desired properties. Examples of suitable fillers include among others glass fibres, polytetrafluorethylene, pigments, fillers and polyamides.

The invention also relates to a process of preparing food, comprising the steps of locating food in an article as defined above and heating the food whilst in said article within an oven. The oven may have a thermal heat

source, or a microwave heat source. The invention also relates to food prepared by such a method.

5 The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise indicated. These nonlimiting Examples are illustrative of certain embodiments designed to teach those skilled in the art how to practice the invention and to represent the best mode contemplated for carrying out the invention.

EXAMPLE I

10 250 g of a mixture consisting of 40% o-terphenyl and 60% m-terphenyl was charged into a four-necked, round bottom flask fitted with a stirrer, a nitrogen inlet a thermometer and a distilling head leading to a condenser. The distilling head was externally wound with electrical resistance heating wire in order that it could be heated and a heating mantle
15 was provided to heat the flask and its contents. The contents of the flask were melted by heating to about 60°C., whereupon 68 g of p-acetoxybenzoic acid were added with stirring. The entire condensation was carried out with constant stirring and with a slow flow of nitrogen through the flask to provide a non-oxidizing atmosphere. The distilling head was heated to
20 about 120°C and the mixture in the flask was heated to about 340°C, polyester precipitation starting to occur at about 300°C. The distilling head temperature was then raised to about 180°C to avoid refluxing of the distillate and/or solidification thereof in the distilling head, and the mixture in the flask was held at about 340°C for about 12 hours. A total of 25.5 g of
25 distillate was collected, consisting primarily of acetic acid, the remainder being primarily terphenyl liquid heat transfer medium. It was observed that 25 g of this distillate were collected within 35 minutes after the temperature of 340°C had been reached, indicating that the polymerization was already approaching completion within this time.

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The resulting mixture was cooled to 80°C, becoming quite viscous. About 200 ml of acetone were added slowly and the mixture was filtered to recover the polyester precipitate. The polyester was extracted overnight with

acetone in a Soxhlet extractor to remove any residual terphenyl liquid heat transfer medium and was then dried in vacuum for 3 hours at 110°C. A yield of 43 g (96% of theory) of p-oxybenzoyl polyester powder was obtained.

5 The product was infusible and upon being held at 400°C in air it exhibited a weight loss of only 0.83% per hour. Differential thermal analysis revealed an endotherm, during heating, at 329-343°C, with a peak at 336°C and a corresponding exotherm during cooling, 10 evidencing a reversible crystalline transition. This reversible transition was also evidenced by a marked change which occurred in the X-ray powder diffraction pattern upon heating the product to about 340°C, the original pattern being resumed upon cooling.

15 In the X-ray powder diffraction pattern of the product at room temperature, using monochromatic copper K-alpha radiation, the large number and the sharpness of the diffraction lines indicated that the polyester was highly crystalline.

20 The use of a liquid heat transfer medium is essential to the method employed. The liquid must be inert, i.e. it must be non-reactive with the p-acetoxybenzoic acid monomer and the condensation products thereof under the conditions employed. The liquid must also be high boiling, having a 25 boiling point under the conditions employed which is at least as high as the highest temperature to which the reaction mixture is heated, and conveniently somewhat higher so that refluxing may be avoided. It will be apparent that the heat transfer medium need not be liquid 30 at room temperature, but it should preferably have a melting point below that of the monomer (about 180°C). A wide variety of materials has been found to be suitable as liquid heat transfer media including, for example, o-terphenyl, m-terphenyl, p-terphenyl and mixtures of two 35 or more thereof such as employed in the Example, partially hydrogenated terphenyls such as those commercially available under the Registered Trade Mark "Therminol 66"; and a

eutectic mixture of 73.5% diphenyl oxide and 26.5% diphenyl such as that which is commercially available under the R.T.M. "Dowtherm A" heat transfer medium. Other suitable liquid heat transfer media include diphenoxybi-
 5 phenyls and mixtures thereof such as those disclosed in U.S. Patent Specification No. 3,406,207.

EXAMPLE 2

This Example illustrates the synthesis of a copolyester useful in the present invention.

10 The following quantities of the following ingredients were combined as indicated.

Item	Ingredient	Quantity	
		Grams	Moles
A	P-hydroxybenzoic Acid	138	1
15 B	Phenyl acetate	170	1.25
C	Therminol 77 (R.T.M)	500	--
D	Diphenyl Terephthalate	318	1
E	Hydrogen Chloride	---	--
F	Hydroquinone	111	1.01
20 G	Therminol 77 (R.T.M)	500	--

Items A - D were charged to a four-necked, round bottom flask fitted with a thermometer, a stirrer, a combined nitrogen and HCl inlet and an outlet connected
 25 to a condenser. Nitrogen was passed slowly through the inlet. The flask and its contents were heated to 180°C whereupon HCl was bubbled through the reaction mixture. The outlet head temperature was kept at 110° - 120°C by external heating during the p-hydroxybenzoic acid, phenyl
 30 acetate ester exchange reaction.

The flask and its contents were stirred at 180°C for 6 hours whereupon the HCl was shut off, the outlet head temperature raised to 180° - 190°C and the mixture stirred
 35 at 220°C for 3.5 hours. Up to this point, 159 grams of distillate were collected in the condenser. Item F was then added and the temperature gradually increased from 220°C to 320°C over a period of 10 hours (10°C/hr).

Stirring was continued at 320°C for 16 hours and then for three additional hours at 340°C to form a slurry. The total amount of distillate, consisting of phenol, acetic acid and phenyl acetate, amounted to 384 g. Item G was added and the reaction mixture permitted to cool to 70°C. Acetone (750 ml) was added and the slurry filtered, the solids were extracted in a Soxhlet with acetone to remove items C and G. The solids were dried in vacuo at 110°C overnight and recovered as a granular powder. In one experiment the resultant copolyester amounted to 320 g, 89.2 percent of theory.

The oxybenzoyl polyesters, discussed generally in the earlier part of this specification and specifically illustrated in Examples 1 to 5, can be moulded according to conventional techniques to produce ovenware articles in accordance with the present invention. Additives such as are conventionally employed in moulding compositions can be incorporated prior to moulding for their recognised purpose. U.S. Patent Specifications Nos. 3,884,876 and 3,980,749 disclose moulding procedures for oxybenzoyl polyesters which could be adapted for the fabrication of ovenware.

EXAMPLE 3

518 parts of isophthalic acid, 1,557 parts of terephthalic acid, 5,175 parts of para-hydroxybenzoic acid, 6,885 parts of acetic anhydride and 2,325 parts of p,p'-bisphenol were mixed together and refluxed for 17 hours, at a temperature of about 180°C, after which the reflux condenser was replaced with a distilling head and the temperature was raised to 345°C over a period of 1½ hours. The reaction mixture was stirred throughout the heating period, being particularly actively mixed during the period in which the temperature was being raised to 345°C. The yield of polymer was 8,020 parts and 8,010 parts of distillate were recovered. The contents of the reaction vessel were removed, cooled and ground to particle sizes in the 20 to 160 mesh range, U.S. Standard Sieve Series.

The resin made was of a molecular weight in the 5,000 - 20,000 range, with an average weight in about the middle of this range. The product was estimated to be about 50% crystalline.

- 5 The resin particles were held under partial vacuum illustratively at an elevated temperature at an absolute pressure of about 100 mm of mercury for eight hours and recovered as a granular powder.

EXAMPLE 4

- 10 The following quantities of the following ingredients were combined as indicated.

Item	Ingredient	Quantity	
		Grams	Moles
A	Terephthalic Acid	291	1.75
15 B	P-Hydroxybenzoic Acid	483	3.50
C	p,p'-biphenol	325	1.75
D	Acetic Anhydride	755	7.40

- 20 Items A-D were heated to 145° and refluxed overnight. The reflux condenser was removed and a distilling head put in place. The mixture was heated with stirring at a rate of 20°C/hour to 300°C and the contents of the reactor removed. At this point about 92-98% of the theoretical acetic acid was collected. The prepolymer was ground up and advanced as in Example 3, employing a temperature of about 250-350°C.

EXAMPLE 5

Item	Ingredient	Quantity	
		Grams	Moles
30 A	p-Hydroxybenzoic Acid	276.	(2.00)
B	Terephthaloyl Chloride	203	1.0
C	Trimesic Acid	8.4	0.040
D	Therminol 66 (R.T.M.)	1274	
E	p,p'-biphenol	186	1.0
35 F	Acetic Anhydride	224.6	2.2

Items A-D were heated to 130°C and held one hour.

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The reaction is exothermic and care was taken to maintain temperature at 130°C. The contents were then heated at 155°C for one hour and 180°C for 4 hours. The mixture was then cooled to 150°C and item E added whereby the temperature was further reduced to 140°C. Item F was then added. This mixture was then refluxed for one hour at 155°C and the reflux condenser replaced by a distillation column. While distilling the acetic acid formed, the contents of the reactor were heated to 330°C and held for 3 hours. The suspended polymer was cooled to 250°C and the mixture passed through a filter. The solid material was worked with trichloroethylene to remove the heat transfer fluid. The dried powder was advanced further in vacuum as in Example 3.

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In order to demonstrate the unique suitability of oxybenzoyl polyesters for the fabrication of ovenware, the following tests were carried out on various items of plastic ovenware, such as bowls, cups, etc., which were fabricated from oxybenzoyl polyesters, polysulphone, polybutylene terephthalate, polypropylene, polycarbonate and a thermoset polyester.

EXAMPLE 6

Thermal (Electric) Oven "No Load" Test

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The plastics article was placed in a glass container on the shelf 14 cm from the bottom of the oven. The oven temperature was set and the oven allowed to heat up from room temperature. The plastics article was allowed to stay 1/2 hour in the oven or to failure, if sooner.

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The following results were noted. A cup cut from a muffin pan fabricated from a thermoset polyester resin emitted an odour within 15 minutes and began to smoke in 30 minutes at an oven temperature of 210°C (410°F). A 5 cm strip cut from a bacon tray fabricated from a polysulphone resin softened in 15 minutes and became totally distorted at an oven temperature at 210°C (410°F). A 5 cm strip from a roasting tray fabricated from a polycarbonate resin softened, sagged and became totally distorted in 10 minutes at an oven temperature of 210°C (410°F).

A bowl made from polypropylene resin melted flat within 10 minutes at an oven temperature of 210°C (410°F). A casserole dish fabricated from polybutylene terephthalate began to smoke in 5 minutes and emitted detectable odour but did not become distorted in 30 minutes at a temperature of 210°C (410°F). A bowl fabricated from an oxybenzoyl polyester, in accordance with the present invention, showed no sign of damage after 1 hour at an oven temperature of 260°C of (500°F).

EXAMPLE 7

Microwave Oven - "No Load" Test

In conducting this test, the plastics object was placed in the centre of the microwave oven directly on the glass tray. The plastics article was heated at full power for 20 minutes or to failure, if sooner.

The following results were noted. A cup cut from a muffin pan fabricated from a filled thermoset polyester emitted a slight odour within 17 minutes, but otherwise showed no sign of damage. A 22.5 cm cake pan fabricated from polypropylene showed no damage other than a softening on the bottom where the rim contacted the hot glass tray. A cup cut from a muffin pan fabricated from polybutylene terephthalate had a hole burned in the side and bottom within 11 minutes. A roasting rack fabricated from a polycarbonate resin showed a distorted spot, 1.5 cm in diameter in the middle of the rack. A bacon roaster fabricated from a polysulphone udel resin showed no damage of any kind. A bowl fabricated from a clear polysulfone udel resin exhibited a discolouration within the surface at the bottom of the bowl. A bowl fabricated from an oxybenzoyl polyester showed no sign of damage of any kind.

EXAMPLE 8

Oil Resistance - Microwave Oven Test

In conducting this test, a layer of Wesson Oil was poured in the plastics vessel. The vessel was centered on the glass tray in the microwave oven. After varying periods at high power, the vessel was removed and examined.

5 The following results were noted. A bowl fabricated from a polypropylene resin showed streaking below the oil line within 6 minutes (severe at 9 minutes). After washing these were shown to be blisters which readily peeled away in fibrous strands. A bowl fabricated from a
10 polysulphone resin exhibited streaking below the oil within 6 minutes which was readily seen. After washing, blisters, cracks and a "burn" spot in the bottom of the bowl were observed. A cup cut from a muffin pan fabricated from polybutylene terephthalate at 5 minutes' exposure
15 showed the side wall at its junction with the bottom bursting and allowing oil to flow out. A slight darkening below the oil was resistant to soap and water. A bowl fabricated from an oxybenzoyl polyester exhibited no observable damage after 20 minutes. The bowl washed
20 clean without stain.

EXAMPLE 9

Freezer To Oven-Thawing-Warming Test

In carrying out this test the plastics containers were loaded with approximately 100 g of Chilli (Shop-Rite
25 canned chilli con carne) and frozen overnight in the freezer section of a refrigerator. The plastics containers were then placed in a tray in 218°C (425°F) preheated oven and allowed to remain until the contents were bubbling. If the container failed, it was removed sooner.

30 The following results were noted. A bowl fabricated from a polypropylene resin had melted to the level of the food after 8 minutes. No thawing had taken place. A bowl fabricated from a polysulphone resin after 27
minutes had a distortion at the lip. At 33 minutes
35 the bowl was soft and distorted. The food was warm, not hot. The bowl cleaned well with no staining. A cook pan fabricated from polybutylene terephthalate had distorted

sides after 12 minutes. At 20 minutes the article was completely out of shape and the food was not warm. The pan was fairly easy to clean but showed slight staining. A cook pan fabricated from a thermoset polyester took 35 minutes to heat the food. The pan was hard to clean. There was a slight stain. A bowl fabricated from an oxybenzoyl polyester showed no damage after 40 minutes to bubbling. The bowl cleaned easily with no staining.

Example 10

Stain and After-Odour Test (Barbecue Sauce)

In conducting this test barbecue sauce was placed in a 1cm layer on the bottom of the plastic container. The container was then placed in a 204°C (400°F) preheated oven for 1/2 hour. At this time the sauce was thick, dark and crusty. After cooling the container was washed with soap and water using a Dobie pad. The container was examined for a stain line and was judged to be stained if 15 minutes further washing could not remove evidence of the stain. The container was then returned to the oven for 15 minutes, removed and smelled while hot. Any unusual odour was noted.

The following results were noted. A cup cut from a muffin pan fabricated from a thermoset polyester exhibited a severe yellow stain. An after-odour of barbecue sauce was detected. A cup cut from a muffin pan fabricated from polybutylene terephthalate exhibited a severe yellow stain. An after-odour was present, although not identified, which could be polymer. A bowl fabricated from a polysulphone resin emitted a slight detectable odour. A bowl fabricated from an oxybenzoyl polyester showed no stain nor after-odour.

The polyester items employed in the tests set forth in Examples 6 to 10 were fabricated from the polyester of Example 3.

Similar tests carried out on the items fabricated from the polyesters of Examples 1, 2, 4 and 5 gave

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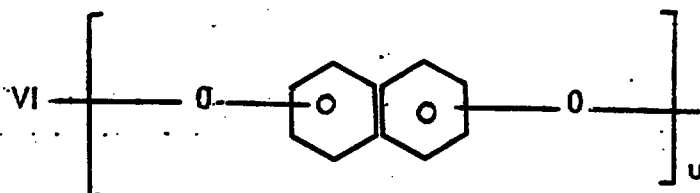
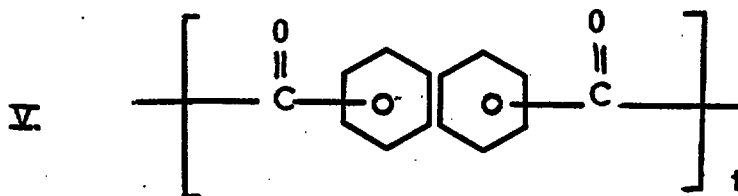
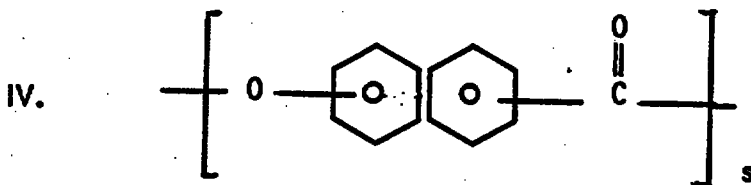
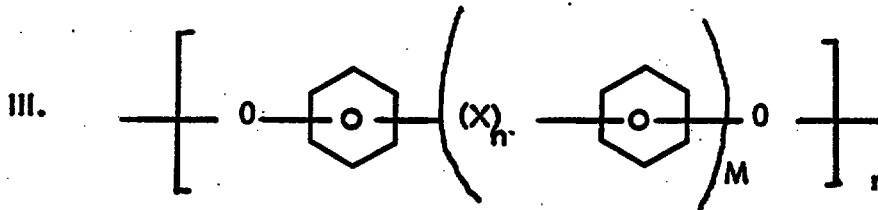
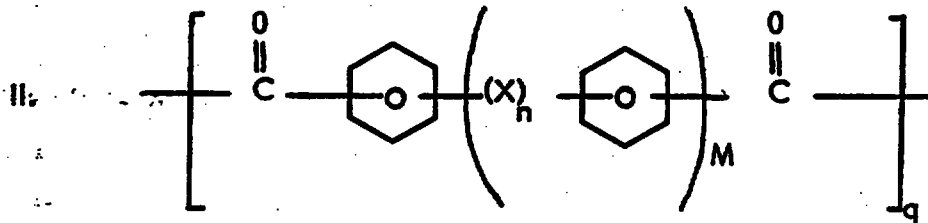
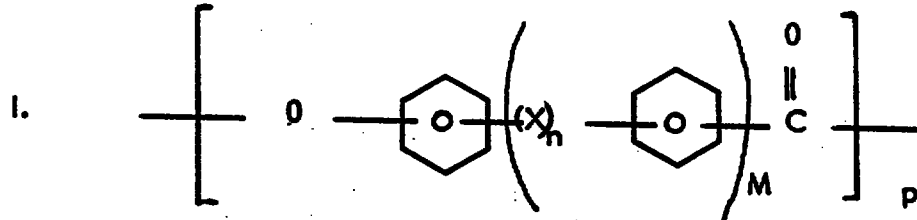
comparable excellent results



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CLAIMS:

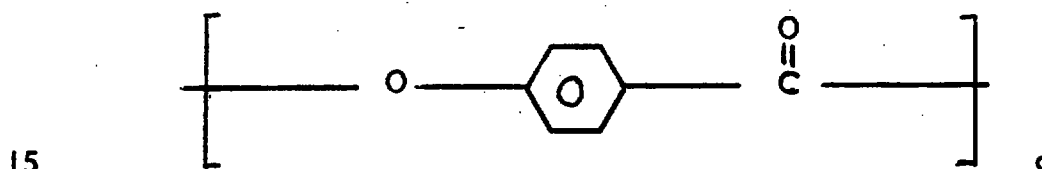
1. A permanent article of ovenware capable of repeated usage comprising a moulded polyester containing recurrent moieties of one or more of the following formulae:



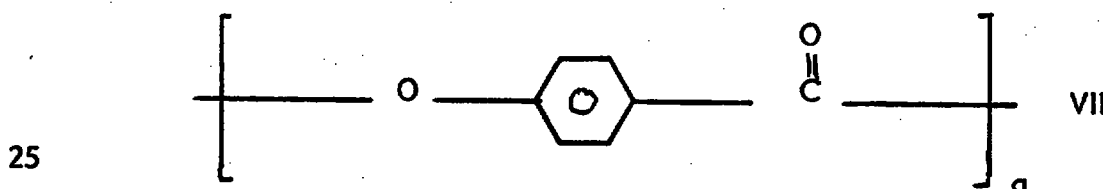


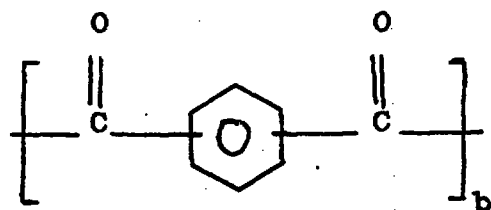
where X is, in any given formula, O, S, C=O, NH, or SO₂, n=0 or 1, m=0 or 1, and the total of the integers p+q+r+s+t+u in the moieties present is from 3 to 800.

- 5 2. An article according to claim 1 in which the ratios of q/r, q/u, t/r, t/u, q+t/r+u and t/t+u are each from 10/11 to 11/10.
3. An article according to claim 2 in which the ratio is 10/10.
- 10 4. An article according to any one of claims 1 to 3, wherein the polyester comprises recurrent moieties of the following formula;



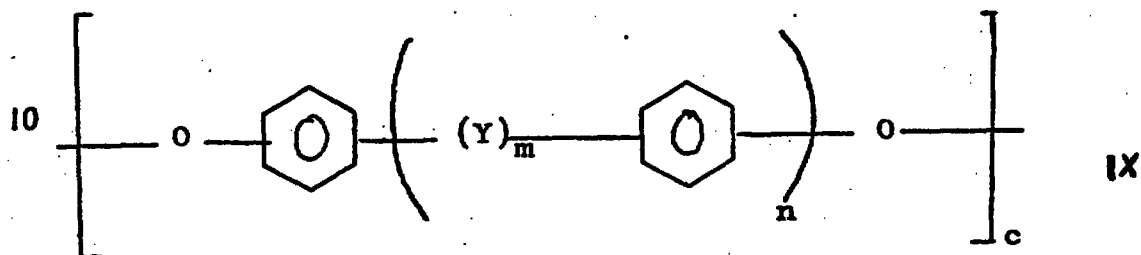
5. An article of ovenware according to any one of the preceding claims comprising a moulded polyester having recurring units of each of Formulate VII, VIII and IX;





VIII

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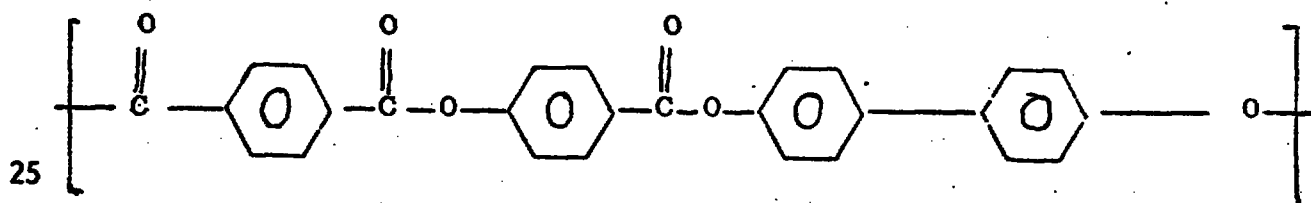
IX

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wherein Y is O or SO₂; m is 0 or 1; n is 0 or 1, b:c is between 10:15 and 15:10; a:b is between 1:100 and 100:1; a+b+c = 3 to 600; the carbonyl groups of the moiety of Formula VII or VIII are linked to the oxy groups of the moiety of Formula VII or IX; and the oxy groups of the moiety of Formulae VII or IX are linked to the carbonyl groups of the moiety of Formula VII or VIII.

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6. An article according to any one of the preceding claims comprising a moulded polyester having recurring units of the formula:



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7. An article according to claim 5, wherein m is 0.

8. An article according to claim 5, wherein n is 0.

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9. An article according to claim 5, wherein a+b+c = 20 to 200.

10. A process of preparing food comprising the steps of locating food in an article according to any one of the preceding claims, and heating the food whilst in said article within an oven.

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11. A process according to claim 10 wherein food is heated by means of a thermal heat source.
- 5 12. A process according to claim 10 wherein the food is heated by means of a microwave heat source.
13. Food whenever prepared by a process according to any one of claims 10 to 12.
- 10 14. An article of ovenware substantially as herein described.
15. An article of ovenware made from polyester substantially as herein described with reference to Example 1.
- 15 16. An article of ovenware made from a polyester substantially as herein described with reference to Example 2.
17. An article of ovenware made from polyester substantially as herein described with reference to Example 3.
- 20 18. An article of ovenware made from a polyester substantially as herein described with reference to Example 4.
- 25 19. An article of ovenware made from a polyester substantially as herein described with reference to Example 5.

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