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SYNTHETIC PAPER SHEET OF CHEMICALLY BONDED SYNTHETIC
POLYMER FIBERS AND PROCESS OF MAKING THE SAME
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Fig. 1

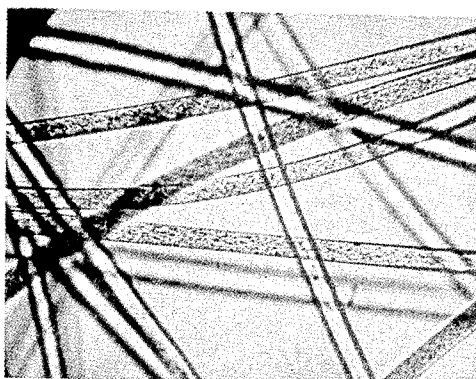
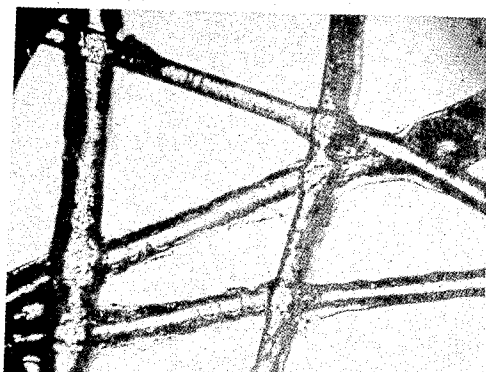


Fig. 2



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SYNTHETIC PAPER SHEET OF CHEMICALLY BONDED SYNTHETIC POLYMER FIBERS AND PROCESS OF MAKING THE SAME

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14 Claims. (Cl. 8—130.1)

This invention relates to a novel article of commerce and to a process for its preparation. More particularly, it is concerned with a paper-like pellicle of a mass of self-bonded, molecularly oriented fiber, produced from a linear synthetic polymer wherein recurring units are linked through amide nitrogen and a process for its production.

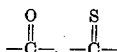
By the expression "... a linear synthetic polymer wherein recurring units are linked through amide nitrogen" is meant a member of the class comprising polyamide, polyurethane, polyurea and polysulfonamide. The nitrogen linkages between the recurring units may be represented as



wherein



is a member of the class consisting of



and



and R is hydrogen, lower alkyl and lower alkylene when the diamine has a ring structure, such as in the case of piperazine.

The failure of synthetic fibers to replace cellulose to any appreciable extent in the past in the manufacture of paper-like structures, despite the inherent desirable properties of the synthetic fibers such as high wet strength, toughness, chemical durability, excellent dimensional stability and the like, is due largely to two factors, namely, the inability of such synthetic fibers to fibrillate, thus rendering them unsuitable for fabrication upon conventional commercial paper-making equipment and also the inability of prior known methods to adequately bond the reticulated mass without loss of desirable fiber properties such as molecular orientation. For instance it has been common in attempts to produce such structures to heat a batt of synthetic fibers under pressure to fuse the matted fibers at points of intersection. Such a product partakes almost completely of the physical properties of a film of a similar synthetic polymer, the molecular orientation having been largely randomized by the heat and necessary plastic flow. Polymer degradation sometimes occurs. A similar effect is obtained when a batt is bonded by partially dissolving it with a solvent and after application of pressure, evaporating off the solvent. Solvent bonding is particularly poor when applied to fibers and/or filaments of synthetic condensation polymers. Other attempts to form such a product have employed various bonding agents to join the crossed fibers in the matted structure. Such a product is limited in its properties by the chemical and physical characteristics of the bonding agent itself and also the adhesive power of the bond for the fiber. Furthermore, when high temperature is re-

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quired to apply the bonding agent, molecular alignment of the fiber suffers.

It is an object of the present invention to provide a paper-like pellicle of a self-bonded, molecularly oriented fiber mass produced from a linear synthetic polymer wherein recurring units are linked through amide nitrogen.

Another object is to provide a process for the preparation of such a paper-like pellicle adaptable to conventional paper-making equipment.

These and other objects will become apparent in the course of the following specification and claims.

In accordance with the present invention a paper-like pellicle of a mass of self-bonded, molecularly oriented fiber produced from a synthetic linear polymer wherein recurring units are linked through amide nitrogen is formed by supplying a solution of join-inducing salt, to be described hereinafter, to the surface of appropriate fibers and/or filaments prior to matting or in a matted form and heating to remove solvent. The resulting paper-like pellicle is self-bonded, i. e., a true joining of fibers and/or filaments at points of intersection is attained without the presence of an added adhesive. Since the joining occurs at a relatively low temperature, the fibers retain molecular alignment. Furthermore, the action of the join inducing salt is a surface phenomenon concentrated at the points of contact of the crossing fibers thereby not substantially affecting the greater portion of the fiber structure. Pressure may be applied during the joining operation to increase compactness of the final product. After formation, the pellicle may be washed free of the join-inducing salt. The product being unitary, self-bonded and molecularly aligned, is both tough and flexible.

The invention will be more readily understood by reference to the drawings.

Figure 1 is a photomicrograph of a fragmentary section of a batt of molecularly oriented fibers produced from a polyamide polymer.

Figure 2 is a photomicrograph of a fragmentary section of a paper-like pellicle produced from the mass of fiber of Figure 1 of the present invention.

In Figure 1, a typical section of a batt of randomly disposed polyhexamethylene adipamide staple is shown. After treatment of the batt in accordance with the present invention a join of the fibers at their points of intersection occurs by virtue of self-bonding, i. e., without benefit of an adhesive, as is shown in the photomicrograph of Figure 2.

In general the mechanics of the process described herein are analagous to those of paper making. Thus the process is readily adaptable to conventional paper-making equipment, although not limited thereto. In one embodiment a batt of fibers is formed on a moving screen. Since the fiber stock can be added from a liquid suspension, the Fourdrinier machine is convenient for this operation. The join-inducing salt can be added to the mixer or showered upon the batt after its formation on the endless screen. Adequate heat and pressure for the join occurs within the felt-drying blanket at the dryer rolls. For the production of a low porosity product, additional heat and pressure may be supplied by passing the batt through a heated calendar roll. The salt may be removed by a water wash at the usual sizing station or the joined mass may be passed through a wash tank. Manufacture may also be performed on the cylinder paper machine by similar modification.

The join inducing salt is a hydrate-forming salt of an inorganic acid, sufficiently soluble in water to yield at least 10% and preferably 30% solutions, the aqueous concentrated solutions being capable of dissolving the synthetic condensation polymer from which the pellicle

is prepared at some temperature up to the boiling point of the salt solution (for example from 0 to 175° C., and generally from 20 to 90° C.). Solubility is readily determined by placing 0.1 gram of the finely divided polymer in 10 ml. of concentrated aqueous salt solution and stirring the mixture, with heating, if necessary, and observing whether the polymer balls up to a coherent mass and/or passes into solution. Soluble low molecular weight polymers tend to pass rapidly into solution, while soluble high molecular weight polymers absorb the salt solution and coalesce before slowly passing into solution.

Among the salts which meet the above definition are included ammonium thiocyanate, lithium thiocyanate, lithium iodide, lithium bromide, sodium thiocyanate, sodium iodide, potassium thiocyanate, magnesium chloride, cupric chloride, calcium thiocyanate, calcium iodide, calcium bromide, zinc iodide, zinc bromide, zinc chloride, ferric chloride, cadmium iodide, and the like. In general these salts are found among the water-soluble thiocyanates, iodides, bromides, and chlorides of group I and II metals of atomic numbers 3 to 48 or compatible mixtures of these salts. The preferred salts are the thiocyanates and chlorides. The preferred cations are ammonium, potassium, sodium, lithium, calcium, magnesium, zinc and ferric iron.

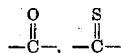
Among the specific polyamides included within the present invention are those formed by the condensation polymerization of a dibasic acid or an amide-forming derivative thereof, such as idipic, sebacic, suberic, azelaic acids or the like, and a diamine such as piperazine, bis-amino cyclohexane, ethylene, tetramethylene, pentamethylene, hexamethylene, decamethylene, para-xylylene diamines or the like. Such materials may also be formed by other well known methods such as by polymerization of amino acids or caprolactam. The fiber-forming polyurethanes are well known and may conveniently be formed by condensation polymerization of a diisocyanate with a glycol. Specific combinations include ethylene glycol, propylene glycol, petaglycol, diethylene glycol and the diisocyanate derivatives of toluylene diamine, ethylenediamine, hexamethylenediamine and the like. As specific exemplifications of polyureas there may be mentioned the polymerization product of carbonyl chloride and piperazine as well as alkylene diamines such as hexamethylene diamine and the like. The polysulfonamides may be prepared by polymerization of disulfonyl chlorides such as meta benzenedisulfonyl chloride with piperazine, an alkylene diamine, such as hexamethylene diamine, and the like. These polymers all contain amide nitrogen linkages, i. e., a linkage of the formula:



wherein



is



or



and R is hydrogen or lower alkyl or lower alkylene when the diamine has a ring structure such as in the case of piperazine. Funicular structures having molecular orientation, such as molecularly oriented fibers, filaments, staple and the like are produced from such polymers by methods well established in the art.

While the join-inducing salt when in concentrated aqueous solution must be capable of dissolving the condensation polymer, it is applied to the fiber batt in a liquid carrier at a concentration, which under the conditions of application has little, or preferably no solvent action upon the fiber. As the liquid carrier is evaporated, the capillary forces at the points of fiber intersection tend to concentrate the join-inducing salt. Thus when the join is made by application of heat upon the substantially dry batt, the action of the salt is concentrated at the points of crossing and the major length of the fiber is unaffected.

The following examples are cited to illustrate the invention. They are not intended to limit it in any manner.

EXAMPLE I

Three grams of $\frac{3}{8}$ inch, 3 denier per filament staple of polyhexamethylene adipamide is suspended in a 6 liter aqueous solution containing 3 grams of sodium carboxymethyl cellulose. The suspension is dispersed on a Rice-Barton "Dyno" pulper having two five-inch concave discs countercurrently stirring at 5000 revolutions per minute at opposite ends of a 5 gallon reservoir. Homogeneity is attained after 2 minutes. Thereafter the aqueous dispersion is filtered over an 8" x 8" square of 80 mesh screen, producing a randomly disposed mat of fibers referred to hereinafter as a "waterleaf." A vacuum of 350 mm. is employed to facilitate moisture removal and to avert bubble entrainment. The waterleaf is gently showered with 20 liters of water to wash out residual sodium carboxymethyl cellulose. 25 cc. of a 10% solution of zinc bromide in water is showered upon the waterleaf. It is thereafter dried at 110° C., pressed under a pressure of 200 p. s. i. at 160° C. for a period of 30 seconds, washed with 3 liters of water to remove zinc bromide and air dried. The resulting paper-like pellicle is self-bonded, has a tensile strength of 32 pounds per inch, a burst strength of 67 pounds per square inch and a tear strength of 1056 grams. All of these tests, as well as those reported hereinafter are made by the standard methods reported in TAPPI Standards. A similarly prepared waterleaf upon which bonding is attempted under the same conditions, but without benefit of the join-inducing zinc bromide salt, has a tensile strength of 0.2 pound per inch, a burst strength of 12.8 pounds per square inch and a tear strength of 200 grams.

Table I below is a summary of various other polyhexamethylene adipamide fiber pellicle preparations illustrating modifications of the process described in Example I.

Table I

Example	Salt	Solvent	Conc. (Percent)	Temp. (° C.)	Press. (lbs./in. ²)	Time (sec.)	Press Cond.	Bond
2	ZnBr ₂	H ₂ O	3.0	160	200	30	Dry	Excel.
3	ZnCl ₂	ETOH	10.0	130	50	30	Wet	V. Good.
4	ZnCl ₂	ETOH	2.5	185	200	30	Wet	V. Good.
5	ZnCl ₂	H ₂ O	10.0	145	200	30	Wet	V. Good.
6	CaCl ₂	H ₂ O	10.0	200	200	30	Wet	V. Good.
7	CaBr ₂	H ₂ O	5.0	160	200	30	Wet	V. Good.
8	Ca(CNS) ₂	H ₂ O	5.0	160	200	30	Dry	Excel.
9	MgCl ₂	H ₂ O	10.0	160	200	30	Dry	Excel.
10	Na(CNS)	H ₂ O	10.0	160	200	30	Dry	Excel.
11	CuCl ₂	H ₂ O	10.0	160	200	30	Dry	Good.
12	FeCl ₃	ETOH	10.0	160	200	30	Wet	Good.
13	LiBr	H ₂ O	5.0	160	200	30	Dry	V. Good.
14	Mg(CNS) ₂	H ₂ O	-----	160	200	30	Dry	V. Good.

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The mechanical properties of the pellicles of Table I are reported in Table II.

Table II

Exam.	Tensile Strength, lbs./in.	Elongation	Burst Strength, p. s. i.	Tear Strength, grams
2	18.0	11.3	58.0	450
3	24.0	10.5	49.0	1,080
4	14.0	7.6	37.7	1,488
5	30.6	14.8	66.0	1,056
6	8.6	6.04	66.1	1,488
7	6.7	7.92	53.2	576
8	24.0	11.7	54.6	1,040
9	14.7	13.6	52.1	617
10	20.8	17.7	65.0	160
11	7.0	7.6	49.0	495
12	9.0	6.5	64.0	583
13	26.0	11.0	65.0	1,461
14	24.0	11.5	58.0	1,030

EXAMPLE 15

A $\frac{1}{2}$ inch, 3 denier per filament staple of a copolymer of 2,5-dimethylpiperazine, with a mixture of 65% terephthaloyl chloride and 35% ethylene bischloroformate is formed by the process described in Example 12 of copending U. S. application No. 359,975, filed June 5, 1953, in the name of Langsdorf and Wittbecker. Three grams of this staple is used to form a pellicle following the technique of Example 1 of the present application, employing calcium thiocyanate as the join-inducing salt as a 2.5% aqueous solution. The batt is pressed at 160° C. under 200 pounds per square inch for 30 seconds. The product is strong, soft and flexible. It has a burst strength of 105 pounds per square inch.

EXAMPLE 16

A $\frac{1}{2}$ inch, 3 denier per filament staple of a polysulfonamide is formed from the polymer prepared by the process described in Example 5 of copending U. S. application No. 252,711, filed October 23, 1951, in the name of Speck. This staple is substituted in the process of Example 15 described above. The product is soft and pliable. It has a burst strength of 70 pounds per square inch and a tear strength of 500 grams.

EXAMPLE 17

A $\frac{1}{2}$ inch, 3 denier per filament staple of polyamide is formed from a polymer produced by the polymerization of caprolactam. Substitution of this staple in the process of Example 15 yields a product having a burst strength of 150 pounds per square inch and a tear strength of 256 grams.

EXAMPLE 18

Six grams of $\frac{5}{8}$ inch, 1 denier per filament staple formed from polyhexamethylene adipamide is suspended in six liters of water containing 30 grams of carboxymethylcellulose (as thickener). A sheet of fibers six inches square is formed. This leaf is then dipped in an aqueous solution containing 20% by weight calcium chloride. Excess liquid is wrung from the leaf. It is pressed wet for 30 seconds under 200 pounds per square inch at 170° C. A dry, pliable film results, having a burst strength of 365 pounds per square inch, a tear strength of 1520 grams and a tensile strength of 16 pounds per square inch.

The following example illustrates the formation of a continuous sheet on a Fourdrinier machine.

EXAMPLE 19

A staple feed is prepared by beating an aqueous suspension of $\frac{5}{8}$ inch, 3 denier per filament staple produced from polyhexamethylene adipamide in a tugboat type beater for 15 minutes. The staple length is thereby reduced to an average of $\frac{1}{4}$ inch. The suspending liquid also contains 0.2% by weight based on the solution of sodium lauryl sulfate (as a wetting agent) and 4% by weight calcium thiocyanate as a join-inducing

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salt. The suspension is fed to a small Fourdrinier machine (Franklin Institute, Philadelphia, Pa.) to produce a well-formed sheet. The machine has an 8 inch screen and is run at 6 feet per minute. As the sheet leaves the screen a squeeze roll removes excess liquid. It progresses through the drying felt over electrically heated rolls regulated at about 140° C. The product is run through a water bath to remove the salt. It is soft, pliable and strong.

The method employed in forming the batt is not critical. It is not necessary that the molecularly oriented fibers be suspended in a liquid and beaten prior to batt formation since adherence among the fibers does not depend on fibrillation as is the case in cellulose paper manufacture. However, to attain uniform distribution it is convenient to suspend a known weight of fibers or the like in a measured quantity of liquid and agitate. Machines used in paper-making such as the Hollander beater, the Tugboat pulper, jordan and the like are all suitable. To assist dispersion the viscosity of the liquid may be raised. This may be accomplished by supplying an additive to water such as sodium carboxymethyl cellulose, partially hydrolyzed polyvinyl acetate (such as "Elvanol 72-51" manufactured by E. I. du Pont de Nemours & Co. of Wilmington, Delaware) the condensation product of ethanolamine with mixed long chain acids (such as "Ninol 2012A," manufactured by Ninol Laboratories of Chicago, Illinois), or the like, or by employing a high viscosity liquid such as glycerine, ethylene glycol, t-butyl alcohol or the like. The optimum viscosity will vary with the type of mixing or beating, the fiber denier, and similar factors. In choosing the suspending media and thickener, therefore, care must be exercised to avoid substances which cannot be subsequently removed from the formed batt with ease since certain foreign substances such as for instance sodium carboxymethyl cellulose, even in minute concentrations, have been found to interfere with the formation of the join. In batt formation from a liquid suspension the use of staple having a length below about 1 inch with a denier per filament within the range of from about $\frac{1}{10}$ to about 6 is preferred. However these values may vary. Fibers of mixed length and denier are suitable. Fibers as short as $\frac{3}{16}$ inch are satisfactory. Instead of laying the batt from liquid suspension, staple, fiber or filament in wet or dry condition may be blown or dopped upon a surface, or a continuous filament may be crossed lapped on a surface. The funicular structure may be crimped or uncrimped and of circular or irregular cross section. The join-inducing salt may be applied to the funicular feed at any stage prior to the joining step. It is sometimes convenient to add it to the beater in which the batt-forming fibers are suspended. When it is desirable to wash the batt after its formation, the salt may be added after the wash step. As previously described, the salt containing solution applied to the batt or leaf is sufficiently dilute to avoid any substantial degradation and/or solution of the fiber structure. The maximum concentration will vary according to the salt employed and the conditions under which it is applied. In general a salt solution sufficient to deposit at least about 10% by weight of salt based on the fabric weight is desirable. A batt wherein salt constitutes by weight of from about 20% to about 30% is preferred. The join step is generally accomplished by exposing the batt of fiber bearing the join-inducing salt to elevated temperature. The optimum temperature will vary with the salt used, the amount of salt employed, the pressure upon the batt and the period of exposure. For a contact period of about thirty seconds a temperature within the range of from about 90 to about 170° C. is usually adequate. While longer heating periods when operating within this temperature range may be employed without deleterious effects, short periods of three minutes or less are preferred to facilitate commercial operations.

Temperatures sufficient to induce molecular randomization cause a weakening of the product and loss of flexibility. For the production of a high strength, hard surface paper-like pellicle, a pressure within a range of from about 50 to about 200 pounds per square inch is usually employed. A lower pressure (0 to 5 lbs) produces a bulkier product of softer surface.

The batt containing salt can be exposed to elevated temperature, preferably in a press as previously discussed, either in the moist or dry condition (i. e. after evaporation of solvent in which the join-inducing salt is applied). Generally it has been found that a stronger join results following a dry press technique.

After the join is complete, the join-inducing salt is washed from the self-bonded coherent mass. The product is a tough, flexible, coherent paper-like pellicle. It is useful in the making of paper money, as a filter media, as a non-woven fabric, in the manufacture of reinforced plastic, as body armor, condenser paper, in high frequency electronic circuits, printed electrical circuits, stencils, permanent ledger, wall-paper and the like. While the invention has been exemplified in the production of flat structures, it is obvious that shaped articles may be similarly formed by depositing the batt or leaf over a form and thereafter applying the necessary heat and pressure. Thus seamless cones, bags, apparel and the like may be made.

A fold endurance rating of about 52,000 is observed when the pellicle of the present invention is tested on an M. I. T. Folding Endurance Tester (Manufactured by Tinius Olsen Testing Machine Company of Willow Grove, Pennsylvania). This compares with a rating of about 1200 for a high grade of kraft paper.

The following example is cited to illustrate utility.

EXAMPLE 20

The pellicle produced in accordance with the directions of Example 1 is folded into conical shape and employed to remove suspended solids from a 50% aqueous sodium hydroxide solution. Filtration is rapid. No deleterious effect upon the folded pellicle is observed.

In summary the process of the present invention comprises heating to a temperature within a range of from about 90° C. to about 170° C. a batt of a molecularly oriented fiber produced from a linear, synthetic polymer wherein recurring units are linked through amide nitrogen, the said batt bearing at the points of fiber intersection a join-inducing salt as previously defined, which salt is originally applied to the said fiber at a concentration at which it is substantially innocuous to the said fiber. The product may be conveniently defined as a paper-like pellicle of a mass of self-bonded, molecularly oriented fiber produced from a linear, synthetic polymer wherein recurring units are linked through amide nitrogen, the said fiber bridged between points of fiber intersection possessing substantially its "as-formed" characteristics.

Many equivalent modifications within the inventive concept will be apparent to those skilled in the art from a reading of the foregoing description without a departure from the inventive concept.

What is claimed is:

1. A synthetic paper sheet composed of a batt consisting essentially of a mass of reticulated molecularly oriented fiber, the said fiber being composed of a fiber-forming linear, synthetic polymer wherein recurring units are linked through amide nitrogen to provide a recurring linkage from the class consisting of a polyamide, a polyurethane, a polyurea and a polysulfonamide, the said recurring linkage being an integral part of the polymer chain, the said fibers being self-bonded only at the points where the fibers intersect each other, the said self-bond having been accomplished by a join-inducing salt, those portions of the fibers between the points of fiber intersection possessing substantially the

same physical and chemical characteristics as they possessed prior to the formation of the bonds.

2. A process of making a synthetic paper sheet which comprises applying, to a batt of reticulated molecularly oriented fiber, the said fiber being composed of fiber-forming linear, synthetic polymer wherein recurring units are linked through amide nitrogen, to provide a polymer from the class consisting of a polyamide, a polyurethane, a polyurea and a polysulfonamide, the said recurring amide nitrogen being an integral part of the polymer chain, a solution consisting essentially of a join-inducing salt for said fibers, the said salt being a hydrate-forming salt of an inorganic acid sufficiently soluble in water to yield at least 10% solutions, the said solution being initially at a concentration sufficiently dilute to avoid substantially altering the physical and chemical properties of the fiber structure, heating the said batt bearing the said dilute salt solution until the salt solution becomes concentrated and located substantially only at the points of fiber intersection, and the fibers are self-bonded to each other at their points of intersection, those portions of the fibers between the points of fiber intersection possessing substantially the same physical and chemical characteristics as they possessed prior to the formation of the bonds, the said heating occurring over a period of at least about 30 seconds and at a temperature within a range of from about 90° C. to about 170° C.

3. The process of claim 2 wherein a pressure of at least about 50 pounds per square inch is applied to the batt during the period of heating.

4. The article of claim 1, wherein the polymer is a polyamide.

5. The article of claim 4 wherein the polymer is hexamethylenedipamide.

6. The article of claim 1 wherein the polymer is a polyurethane.

7. The article of claim 1 wherein the polymer is a polyurea.

8. The article of claim 1 wherein the polymer is a polysulfonamide.

9. The process of claim 2 wherein the solution of the said hydrate-forming salt is applied to the fiber prior to batt formation.

10. The process of claim 2 wherein the solution of the said hydrate-forming salt is applied to the batt after batt formation.

11. The process of claim 2 wherein the heating is performed with the batt under a pressure of from about 50 to about 200 pounds per square inch.

12. The process of claim 11 wherein the heating under pressure is applied to the wet batt.

13. The process of claim 11 wherein the heating under pressure is applied to the batt after removal of moisture by evaporation.

14. The process of claim 2 wherein the said hydrate-forming salt is a water-soluble salt of a metal of the first two groups of the periodic system having atomic numbers from 3 to 48.

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