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EMULSIONS

(57) **Abrégé/Abstract:**

A method of producing a thickened emulsion explosive, which method comprises reacting in an emulsion explosive an amine compound and an α,β -unsaturated carbonyl compound such that thickening of the emulsion explosive occurs.

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AMINE REACTED ALPHA, BETA-UNSATURATED CARBONYL COMPOUND THICKENED EXPLOSIVE EMULSIONS

The present invention relates to emulsion explosives and, in particular, to emulsion explosives with desirable rheology characteristics. The present invention also relates to methods for producing such emulsion explosives, to their use and to methods of blasting that utilise them.

BACKGROUND TO THE INVENTION

Emulsion explosives are widely used in the explosives industry. They include an aqueous oxidizer phase dispersed in a fuel phase, or vice versa. A desirable property of emulsion explosives is that they are of low viscosity during processing and handling but of high viscosity in packaged cartridges or as a bulk product following loading into a borehole. This combination of viscosity properties facilitates efficient processing and provides excellent properties in the field. During processing low viscosities ease pumping, improve the flow of emulsion in pipes and hoses, and minimise adhesion to the walls of tanks and conduits of manufacturing systems. Higher viscosities in packaged products permit good tamping and allow cartridges to be cut cleanly. In bulk explosives high viscosities improve retention in boreholes inclined upwardly and prevent loss of product in cracked ground and in joints. The provision of a highly viscous bulk explosive with enhanced dimensional stability is particularly advantageous. Enhanced dimensional stability lessens stress on detonator leads when loading deep boreholes. It also reduces the likelihood of borehole collapse in soft ground, for example, in tar sands or coal.

The addition of natural wax such as bees wax, petroleum based waxes, polymeric waxes or polymeric resins to emulsion explosives in order to control emulsion rheology is well known. However, the use of such waxes and resins has a number of drawbacks. For example, during production of the emulsion explosive it is necessary to melt the wax or resin into the fuel phase of the emulsion. Accordingly, the rheology of an emulsion explosive that contains wax or resin is temperature dependent in accordance with the physical properties of the wax or resin. This can have practical implications and constraints on the use of such emulsions. In cold conditions the emulsion may be too

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viscous to be pumpable. In hot conditions the emulsion may not be viscous enough for the intended use, such as in inclined or vertical boreholes where product retention is required.

The present invention seeks to provide an alternative to the presently available emulsion explosives thickened using waxes and resins that does not suffer the practical drawbacks discussed above or, at least, a useful alternative thereto.

SUMMARY

Certain exemplary embodiments provide a method of producing a thickened emulsion explosive, which method comprises reacting in an emulsion explosive an amine compound and an α,β -unsaturated carbonyl compound such that thickening of the emulsion explosive occurs, wherein the α,β -unsaturated carbonyl compound is selected from aldehydes, ketones and acrylates.

Certain exemplary embodiments further provide a thickened emulsion explosive containing a thickening agent comprising a reaction product of an amine compound and an α,β -unsaturated carbonyl compound, wherein the α,β -unsaturated carbonyl compound is selected from aldehydes, ketones and acrylates.

Certain exemplary embodiments further provide a method of loading a borehole with a bulk thickened emulsion explosive, which method comprises: introducing an emulsion explosive into the borehole; and reacting in the borehole an amine compound and an α,β -unsaturated carbonyl compound in the emulsion explosive such that thickening of the emulsion explosive occurs, wherein the α,β -unsaturated carbonyl compound is selected from aldehydes, ketones and acrylates.

Certain exemplary embodiments further provide a method of producing a packaged emulsion explosive comprising: reacting in an emulsion explosive an amine compound and an α,β -unsaturated carbonyl compound such that thickening of the emulsion explosive occurs; and packaging the emulsion explosive, wherein the α,β -unsaturated carbonyl compound is selected from aldehydes, ketones and acrylates.

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Accordingly, in a first aspect of the present invention there is provided a method of producing a thickened emulsion explosive, which method comprises reacting in an emulsion explosive an amine compound and an α,β -unsaturated carbonyl compound such that thickening of the emulsion explosive occurs. The invention further provides a thickened emulsion explosive produced in accordance with this method.

In accordance with this aspect of the present invention it has been found that certain amine and α,β -unsaturated carbonyl compounds can be reacted within a pre-formulated emulsion explosive in order to provide a rheological change, namely thickening, of the emulsion explosive. As will be explained in more detail below this rheological change has significant and advantageous practical implications with respect to the use of the emulsion explosive.

In accordance with the first aspect of the invention there is also provided a thickened emulsion explosive produced by the method of the present invention, i.e. containing a thickening agent comprising the reaction product of an amine compound and an α,β -unsaturated carbonyl compound.

Also provided is a method of loading a borehole with a thickened emulsion explosive which comprises introducing an emulsion explosive into the borehole and reacting (in the borehole) an amine compound and an α,β -unsaturated carbonyl compound in the emulsion explosive such that thickening of the emulsion explosive occurs.

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In accordance with the first aspect, further provided is a method of producing a packaged emulsion explosive, which method comprising reacting in an emulsion explosive an amine compound and an α,β -unsaturated carbonyl compound such that thickening of the emulsion explosive occurs, and packaging the emulsion explosive.

In a second aspect of the present invention there is provided a method of producing a thickened emulsion explosive, which method comprises forming an emulsion explosive by mixing an aqueous oxidizer phase, a fuel phase and an amine compound and reacting in the emulsion explosive the amine compound and an α,β -unsaturated carbonyl compound such that thickening of the emulsion explosive occurs. The amine compound and the α,β -unsaturated carbonyl compound are contacted and reacted whilst the emulsion explosive is being mixed in order to form a thickened emulsion explosive. In accordance with this aspect of the invention it has been found that certain amine compounds function as an emulsifier (and as a thickening agent in combination with certain α,β -unsaturated carbonyl compounds), thereby removing the need to use a separate (conventional) emulsifier. The invention also provides a thickened emulsion explosive produced in accordance with this method.

Also provided is a method of loading a borehole with a thickened emulsion explosive which comprises forming an emulsion explosive by mixing an aqueous oxidizer phase, a fuel phase and an amine compound, introducing the emulsion explosive into the borehole and reacting (in the borehole) the amine compound and an α,β -unsaturated carbonyl compound emulsion such that thickening of the emulsion explosive occurs.

Another related aspect provides is a method of producing a packaged emulsion explosive, which method comprises forming an emulsion explosive by mixing an aqueous oxidizer phase, a fuel phase and an amine compound, reacting the amine compound and an α,β -unsaturated carbonyl compound in the emulsion explosive such that thickening of the emulsion explosive occurs, and packaging the resultant emulsion explosive.

Further aspects of the invention provide a use in a blasting operation of a thickened emulsion explosive, and a method of blasting which comprises loading a borehole with a

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thickened emulsion explosive in accordance with the invention, and detonating the thickened emulsion explosive.

BRIEF DESCRIPTION OF THE DRAWINGS

Various embodiments of the invention are described herein, by way of example only, with reference to the following drawings in which:

Figure 1 is a schematic illustrating implementation of an embodiment of the present invention;

Figure 2 is a schematic of a process for producing a packaged thickened emulsion explosive;

Figure 3 is a process flow diagram of a plant for producing a packaged thickened emulsion explosive;

Figure 4 is a graph of the compression test results for Example 4;

Figure 5 is a graph of the compression test results for Example 4;

Figure 6 is a graph of the compression test results for Example 4;

Figure 7 is a graph of the compression test results for Example 12;

Figure 8 is a graph of the compression test results for Example 12; and

Figure 9 is a graph of the compression test results for Example 12.

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DETAILED DESCRIPTION OF THE INVENTION

The first aspect of the present invention is based on the selection of suitable amine and α,β -unsaturated carbonyl compounds that will react with each other in an emulsion explosive to provide a desirable rheological effect, namely thickening of the emulsion explosive. The first aspect requires incorporation of appropriate amine and α,β -unsaturated carbonyl compounds into the emulsion explosive in a suitable manner and in sufficient amounts to achieve a desired thickening of the emulsion explosive.

The degree of thickening that is achieved will depend upon a variety of factors including the selection of the α,β -unsaturated carbonyl compound and the amine compound, the relative proportions of the α,β -unsaturated carbonyl compound and the amine compound to each other and to the other components of the emulsion explosive, and the extent to which the amine and α,β -unsaturated carbonyl compounds are dispersed in the emulsion explosive. These parameters may be varied in order to control the degree of rheological change that takes place in accordance with this aspect of the present invention.

Without wishing to be bound by theory, it is believed that the amine compound and the α,β -unsaturated carbonyl compound react within the body of the emulsion explosive by a Michael-type addition reaction resulting in the formation of a crosslinked polymeric network within the emulsion explosive. It is this crosslinked network that is believed to result in thickening of the (base) emulsion explosive. This may be because the network in some way binds or interacts with molecules of the fuel phase within the emulsion explosive thereby limiting mobility of such molecules. The extent to which this network forms will influence the extent to which the emulsion explosive is thickened. At one extreme the formation of the crosslinked network may be extensive enough to result in a continuous network extending through the emulsion explosive. In all aspects of the present invention, thickening includes polymerization.

The amine and α,β -unsaturated carbonyl compounds, and the amounts thereof, are selected on the basis of suitably reactive combinations. Thus, in the amounts used the amine and α,β -unsaturated carbonyl compounds should react with each other at an appropriate rate at

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the prevailing processing temperature. As will be apparent from following discussion, in embodiments of the first aspect of the invention it may be required for the thickening effect to take place very rapidly, even instantaneously, when the amine and α,β -unsaturated carbonyl compounds are contacted and react with each other. In other embodiments slower reaction of these compounds to achieve thickening may be tolerated.

It is desirable for the reaction between the α,β -unsaturated carbonyl compound and the amine compound to produce little to no exotherm, since significant temperature increases in the emulsion explosive are to be avoided, even if only localised in nature. In addition, the compounds selected should not destabilise or have a detrimental effect upon the properties of the emulsion explosive. In particular, the reaction of the amine and α,β -unsaturated carbonyl compounds should not devalue the detonability or basic explosive energy of the emulsion explosive. In practice, suitable amine and α,β -unsaturated carbonyl compounds and the optimum amounts to be used may be determined experimentally.

In principle, any amine compound and α,β -unsaturated carbonyl compound that undergo a Michael-type addition reaction and that cause thickening of an emulsion explosive may be used in the present invention. However, there are practical constraints as noted above and these must be taken into account when considering compounds to use. The following provides a general description of compounds that are likely to be of use.

To be reactive with each other the amine compound and α,β -unsaturated carbonyl compound must have suitably available and reactive sites. Generally, each compound should have multiple reactive sites so that an extensive crosslinked network can be formed. For this reason it may also be preferred for a reactive site of the amine or α,β -unsaturated carbonyl compound to be capable of reacting with more than one molecule of the complementary reactant. In that case the number of reactive sites per molecule of the respective compound may be reduced whilst retaining high crosslinking ability. For example, a lower degree of substitution may be required in an amine compound substituted with primary amine reactive sites when compared to a compound having secondary amine reactive sites due to the increased capacity of a primary amine to bond

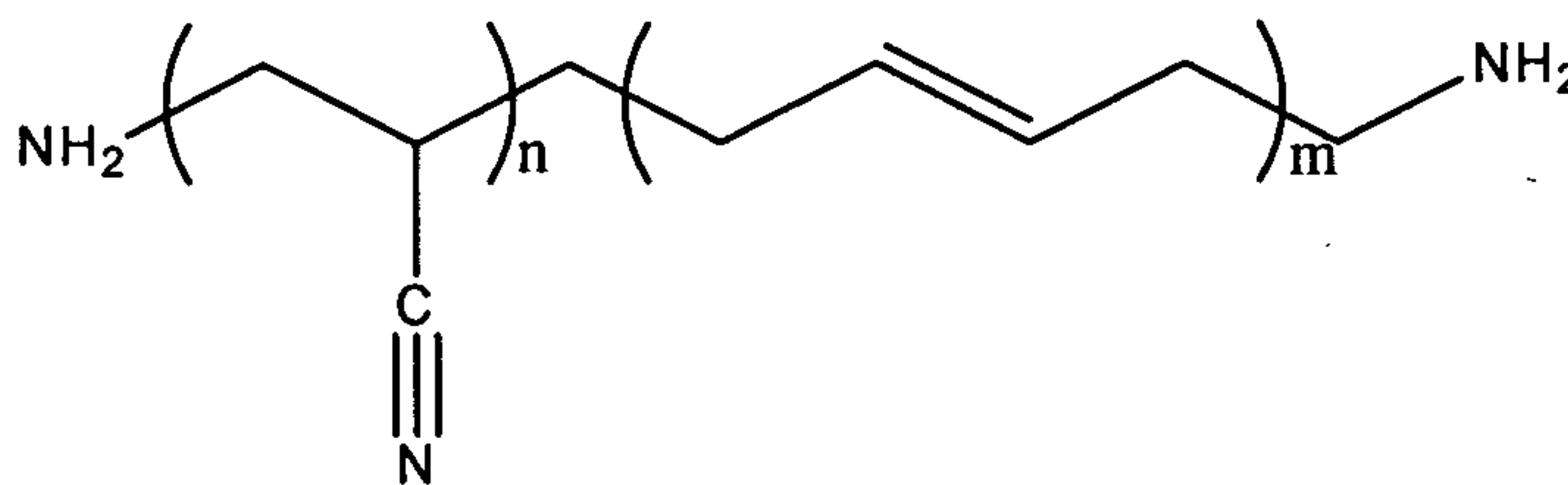
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with an α,β -unsaturated carbonyl compound. Typically, the amine compound will be a polyamine having at least two primary amine functionalities that are suitably reactive towards the α,β -unsaturated carbonyl compound. The latter may also include more than one reactive site viz-a-viz the amine.

Suitably available reactive sites of the compounds are located so that crosslinking reactions are not sterically hindered. In this regard, at least one of the amine or α,β -unsaturated carbonyl compounds is generally substituted with terminal reactive sites. For example, an amine-terminated polymer may be selected as a suitable amine compound. In that case, it is likely to be beneficial, with respect to network formation, that the amine compound include at least two primary amine groups that are reactive toward the α,β -unsaturated carbonyl. Secondary amine functionalities may be present provided they give the requisite reactivity.

The amine compound may also include one or more functionalities that render the amine moieties more nucleophilic and thus reactive with respect to the α,β -unsaturated carbonyl compound. One skilled in the art would be familiar with such functionalities.

Examples of compounds that have been found to be useful in practice of the first aspect of the present invention include amine-terminated butadiene-acrylonitrile copolymers of formula:

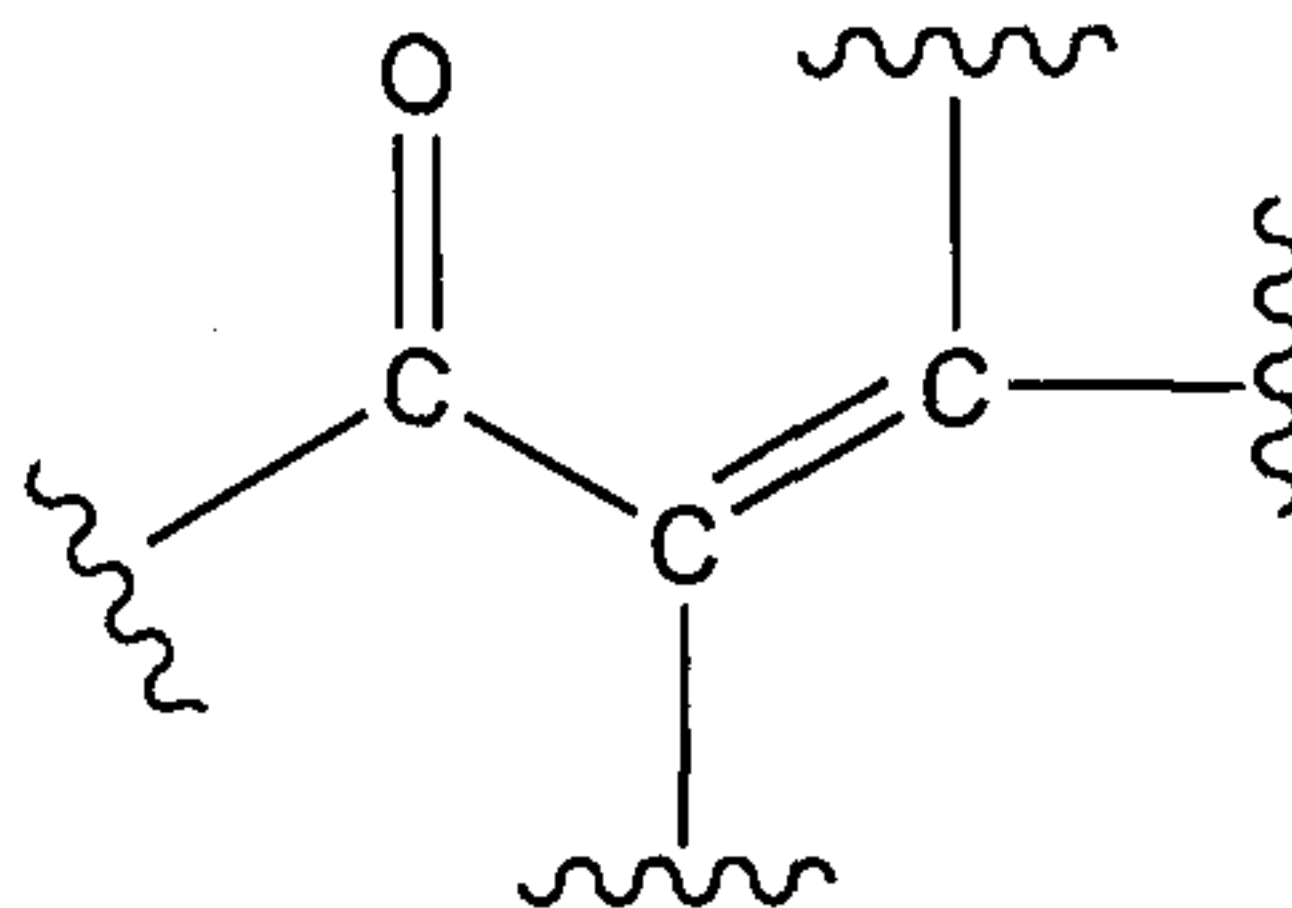


in which m is about 10 - 170 and n is about 2 - 60 and such that the proportion of acrylonitrile in the copolymer can range from about 10-30%. The amine-terminated butadiene-acrylonitrile copolymers found to be useful have molecular weights of approximately 4000. Accordingly, in those embodiments m is around 50-70 and n is

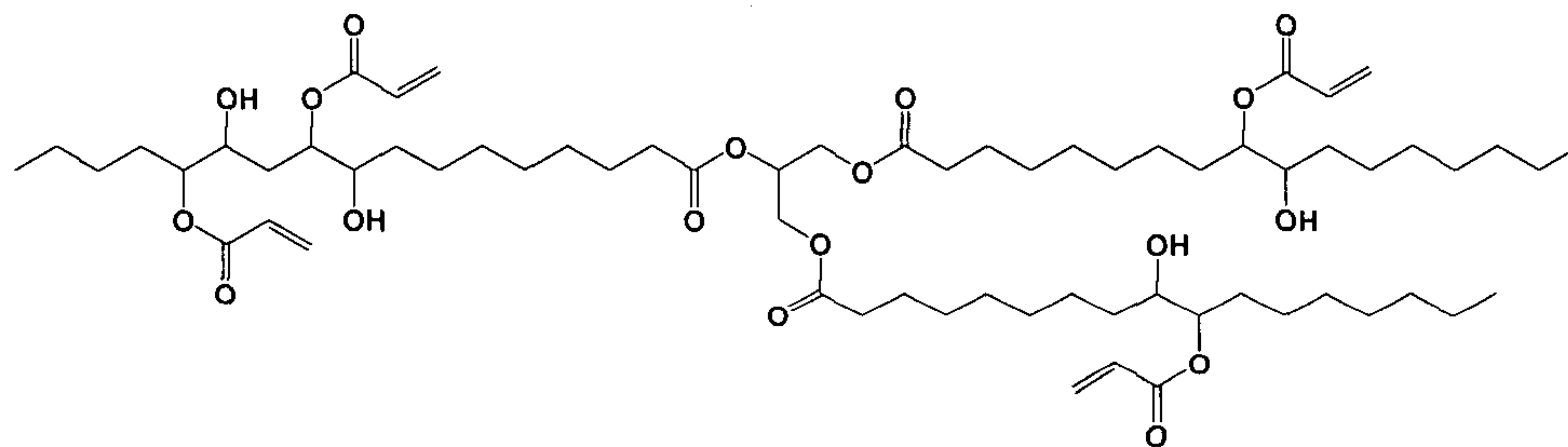
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around 5-25. Such compounds are commercially available, for example Hycar Reactive Liquid Polymer ATBN 1300X21.

The α,β -unsaturated carbonyl compound may be an α,β -unsaturated aldehyde or ketone, or any other Michael-type acceptor. The general structure of an α,β -unsaturated carbonyl compound is shown below.



Examples of readily available compounds that have been found to be useful in practice of the first aspect of the invention include α,β -unsaturated acrylates, such as those derived from epoxidized vegetable oils. Examples of epoxidized vegetable oils include epoxidized soya oil, epoxidized castor oil, epoxidized rape-seed oil and epoxidized linseed oil. The use of epoxidized soy oil acrylate may be preferred. An example of the structure of a typical epoxidized soy oil acrylate is shown below.



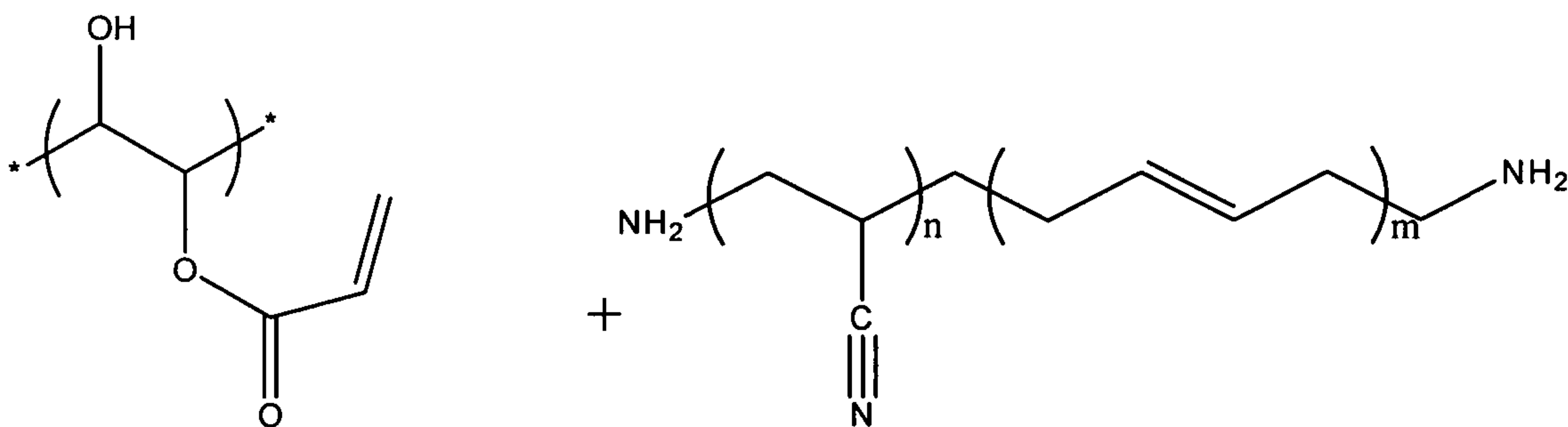
Alternatively, the α,β -unsaturated acrylates may be derived from mineral oils, for example, the α,β -unsaturated acrylates may be an ethoxylated trimethylopropane triacrylate in which the number of ethoxylated groups may be at least three and may be in excess of 20.

In some embodiments it may be desirable to use a polymeric α,β -unsaturated acrylate. Suitable polymeric α,β -unsaturated acrylates may be selected from the group consisting of polyisoprene diacrylate, polybutadiene diacrylate, copolymers thereof and mixtures thereof.

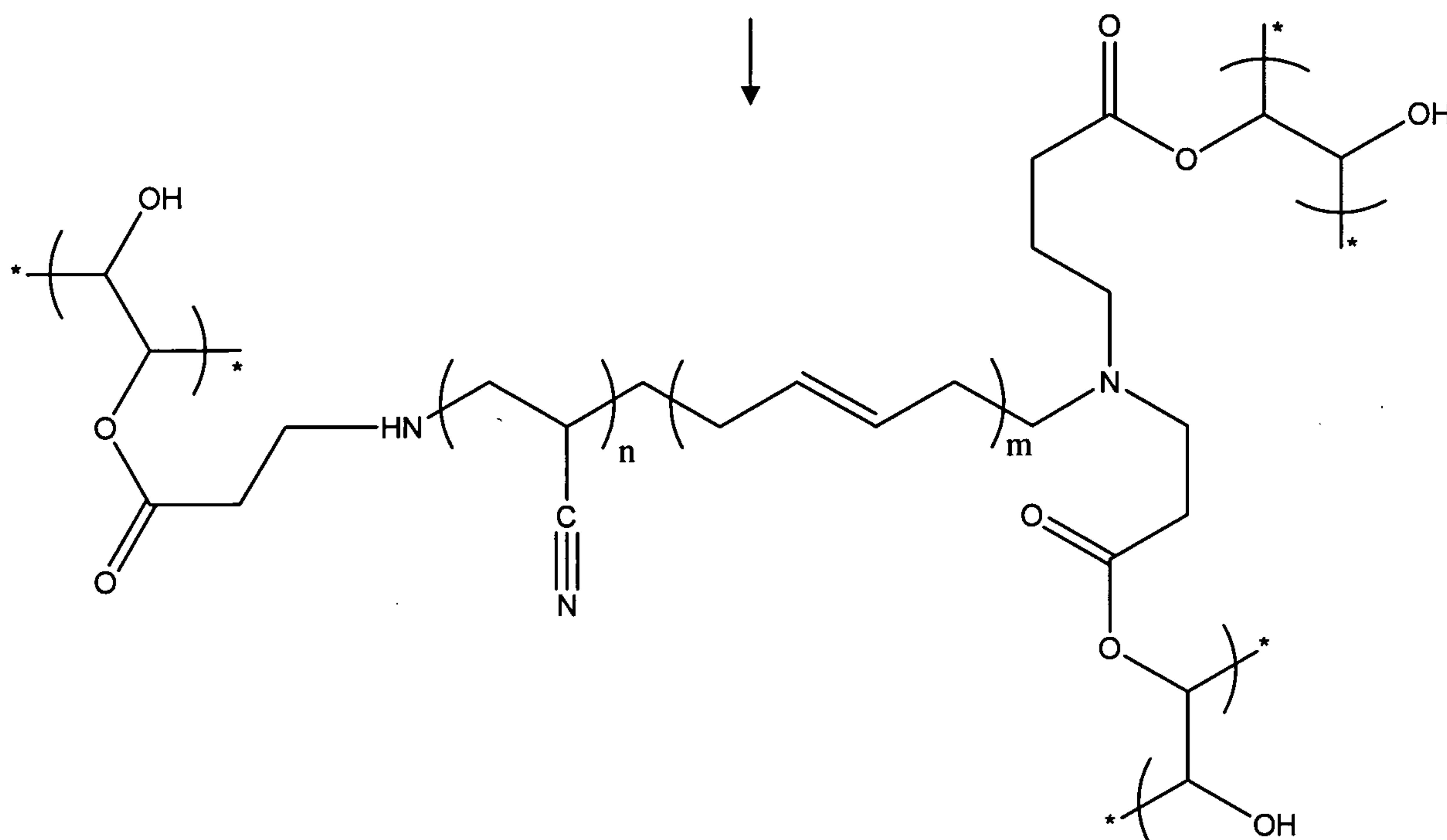
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It is possible to use one or more amine compounds and one or more α,β -unsaturated carbonyl compounds in order to achieve the desired effect in accordance with the first aspect of the present invention.

In some embodiments of the first aspect of the present invention the amine compound is an amine-terminated butadiene-acrylonitrile copolymer of the formula shown below and the α,β -unsaturated carbonyl compound is epoxidized soy oil acrylate of the formula shown below. In this embodiment the value of m is approximately 67 and the value of n is approximately 8. The formula shown below only illustrates a single reactive site of the epoxidized soy oil acrylate. The epoxidized soy oil acrylate may have at least two reactive sites and will typically be derived from epoxidized soy oil with an average of 4.1 - 4.6 epoxy rings per triglyceride molecule. Reaction of these compounds is believed to give a product in which the amine compound is bonded to at least two, preferably three or four, molecules of the acrylate. This is illustrated in the following reaction scheme in which the reaction product includes three moieties derived from the acrylate bound to an amine molecule.



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Usually the first aspect of the present invention is implemented by formulating a modified emulsion composition comprising the amine compound or α,β -unsaturated carbonyl compound, and by introducing into the modified emulsion the complementary reactant when thickening is required. Typically, the amine or α,β -unsaturated carbonyl compound is blended with the fuel component prior to formation of the emulsion, or it may be added externally after the base emulsion explosive has been formed. In the latter case it is likely that the reactant compound will migrate to the fuel phase. The base emulsion may be of conventional type and may be formulated in conventional manner. The emulsion may be an oil-in-water emulsion but the first aspect may have greater applicability in relation to water-in-oil emulsions. Generally, the α,β -unsaturated carbonyl compound will be the reactant that is added to the fuel phase of the emulsion or externally to the emulsion.

The base emulsion or the modified emulsion may be sensitized using conventional methods such as, for example, through the addition of glass or plastic microspheres. It is also possible to add substances or mixtures of substances which are oxygen releasing salts or which are themselves suitable as explosive materials. In addition, the thickened emulsion explosive may be a gassed product and/or the density of the product may be varied as appropriate using known techniques. However, the application of these

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techniques, such as gassing the emulsion explosive, may need to be modified to ensure that adequate modification is performed prior to the completion of the thickening reaction.

For successful implementation of the first aspect of the present invention it is believed to be important that the relevant reactant is thoroughly dispersed in the emulsion explosive composition prior to addition of the complementary reactant. As amine and α,β -unsaturated carbonyl compounds may constitute a relatively small proportions of the emulsion explosive composition, effective mixing may be very important to ensure that the reaction takes place throughout the composition. The appropriate degree of mixing may be achieved through the use of in-line static mixers.

If storage stable, the emulsion explosive composition containing the relevant reactant may be prepared and stored, and possibly transported, as necessary prior to use. If stored it may be desirable to agitate the emulsion explosive composition thoroughly prior to use.

Addition of the amine or α,β -unsaturated carbonyl compound to the base emulsion explosive (and thorough blending therewith) preferably does not cause any significant viscosity increase in itself. Some viscosity change can be tolerated provided it does not make subsequent handling and processing unduly difficult.

The complementary reactant is added to the formulated modified emulsion when the thickening effect is required to take place. At that time it is believed to be important that the complementary reactant is mixed thoroughly into the modified emulsion so that reaction between the amine and α,β -unsaturated compounds takes place throughout the emulsion explosive composition. In this way localised thickening can be avoided.

In order to enhance the ease with which the complementary reactant is dispersed in the modified emulsion it is possible to first dissolve or disperse the reactant into a solvent comprising the fuel as the fuel component, or materials compatible with the fuel component, for example corn oil. The complementary reactant may be combined with the solvent in a 50/50 ratio determined by weight.

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Usually, the ratio by weight of the amine compound to α,β -unsaturated carbonyl compound will be between 10:1 and 1:3, preferably the ratio is around 1:2. Typically, the total weight of amine and α,β -unsaturated carbonyl compounds included or to be included in the emulsion explosive composition will be 0.4-2.5% based on the total weight of the emulsion explosive composition.

The thickened emulsion explosives in accordance with the first aspect of the present invention may be utilised in packaged or bulk explosives suitable for surface or underground applications. The thickened emulsion explosive may be prepared by a number of different methods, depending upon the ultimate use of the product. When preparing packaged product a relatively slow thickening effect may be tolerated with the full extent of the rheological change taking place prior to cutting and packaging. Alternatively, components may be mixed thoroughly just prior to packaging with the thickening effect developing within the packaging.

The thickening reaction will occur at the prevailing temperature used in the production of conventional emulsion explosives. In particular, the thickening reaction may occur across a range of temperatures from about 15°C to about 100°C. The rate of thickening increases with temperature and at the upper end of the temperature range the reaction may be instantaneous. The rate of thickening may also be varied through the addition of a polyvalent inorganic salt or polyvalent organic salt. For example, the addition of calcium nitrate to the emulsion explosive can increase the rate of thickening.

The degree to which the resulting emulsion explosive is thickened can vary. Thickening includes an increase in viscosity and a degree of rheological change up to, and including, the formation of a thickened emulsion explosive with a non-fluid, deformable rheology such as a stiff gel. Typically, the thickened emulsion explosive composition has a viscosity of 40,000 – 1,000,000+ cps, as measured a Brookfield Viscometer using T bar E or F. Preferably, it takes the form of a stiff gel. This property in particular makes the composition of great utility in bulk applications where up-hole retention is required. Embodiments of the thickened emulsion explosive may be thickened to such a degree that it may be possible to cut the stiff gel formed and have the cut product retain its shape.

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Accordingly, it may be possible to further process the composition to form a granulated product. It is of course possible to manipulate the final viscosity as might be required in the field.

Once the thickening reaction has completed, the resulting degree of rheological change can be maintained across a range of temperatures. Thus, it may be possible to expose the thickened emulsion explosive to a broad range of temperatures without any significant reduction in the viscosity of the thickened emulsion explosive. Thus, the ease with which the thickened emulsion explosive may be cut is not usually significantly affected over such temperature ranges. Accordingly, the properties of a thickened emulsion explosive in accordance with the invention may not be sensitive to temperature fluctuations.

When the thickened emulsion explosive is used as a bulk product it is important that the thickening effect takes place within a borehole that is being loaded rather than in the equipment used for formulation and pumping of the bulk product. If thickening takes place within this equipment, loading difficulties and fouling may occur.

When using the thickened emulsion explosive as a bulk product it may be desirable for the thickening effect to take place very rapidly and preferably instantaneously when the respective reactants come into contact with each other within the emulsion explosive. Rapid thickening is especially important when loading up-holes or upwardly included boreholes where product retention is vital. In such cases, if the thickening effect associated with this aspect of the invention is too slow, the bulk product will not be retained in place as required.

In this case, one loading hose may be used to deliver emulsion explosive composition containing one of the reactants into the borehole with a separate loading hose delivering the complementary reactant. Mixing of these individual components as they exit the respective loading hoses may be achieved using a suitable mixing nozzle. In one embodiment the loading hoses may be arranged in parallel along a common axis. In a preferred arrangement one component may be delivered down a loading hose provided as a centre-line within another larger diameter hose, i.e. as a concentric arrangement. In both

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cases a nozzle mixer may be used to thoroughly blend the components as they exit respective loading hoses.

A schematic of a preferred loading hose (10) for the production of a thickened bulk product is shown in Figure 1. In an embodiment, a modified emulsion which comprises a preferred α,β -unsaturated carbonyl compound, epoxidized soy oil acrylate, is pumped from bulk emulsion storage tank (11) using a pump (12) and into the loading hose (10). The complementary reactant, the amine compound, is centre line injected using pump (13) through the complementary reactant line (14) into the loading hose. As the complementary reactant is pumped towards the nozzle (15) of the loading hose (10) it passes through a water ring injector (16). A static mixer (17) is positioned at the nozzle (15) and mixes the modified emulsion and complementary reactant together to form the thickened emulsion explosive.

Alternatively, it is possible to produce a packaged thickened emulsion explosive by producing the modified emulsion at a bulk emulsion plant and then transporting the first component to a packaging facility. The emulsion may be transported to a packaging facility (regional packaged plant) where it may be stored in silos. The product may then be pumped into the blender where it is sensitized. The sensitized emulsion may also be stored in a silo prior to use. At the packaging facility the modified emulsion and complementary reactant are combined to form the thickened product. Alternatively, the base emulsion may be produced at a bulk emulsion plant, then modified through the addition of a reactant at the packaging plant and stored prior to being combined with the complementary reactant.

The thickened emulsion explosive may be packaged to the desired diameter after the emulsion has thickened. Alternatively, the emulsion explosive composition may be packaged as the emulsion thickens. If a significant proportion of any reaction between the amine compound and the α,β -unsaturated carbonyl compound takes place during packaging, infrastructure costs may be reduced by removing the need to use the cooling bath that is often required for the production of explosive compositions thickened using

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waxes. However, in embodiments it may be desirable for the majority of the thickening to occur after packaging.

In some embodiments, it may be desirable to pump the emulsion explosive composition to be packaged into the cartridge production unit using a nozzle similar to the one described above for forming a thickened bulk product. Accordingly, it is possible to prepare the product so that the reactants come into contact with each other as the product is being packaged. Mixing may be achieved using a nozzle mixer at the end of the emulsion explosive loading hose. Thus, the components are blended as they exit the loading hose.

Figure 2 is a schematic of the process used to package the thickened emulsion explosive in accordance with the method previously described. In an embodiment, a modified emulsion which comprises a preferred α,β -unsaturated carbonyl compound, epoxidized soy oil acrylate, is pumped from a bulk emulsion storage tank (18) using a pump (not shown) and into the emulsion line (20). The complementary reactant, the amine compound, is centre line injected using pump (21) through the complementary reactant line (22) into the emulsion line (20). As the components are pumped through the emulsion line (20) into the cartridge production unit (19) they are combined using a static mixer (23) to produce the thickened emulsion explosive. The cartridges of the thickened emulsion explosive are transported by a conveyor belt (24) to the packaging unit (25).

Figure 3 illustrates a process flow diagram of a packaging plant suitable for use in accordance with the method previously described. In an embodiment, a modified emulsion comprising an α,β -unsaturated carbonyl compound, for example a epoxidized soy oil acrylate, is pumped from a production plant transport truck (26) into a bulk emulsion storage tank (28) using a pump (27). Bulk sensitizing agents, including microballoons, other components, such as ammonium nitrate prills and granulated aluminium powder are transferred into respective feed hoppers (29), (30) and (31). These additives agents are then fed into a primary hopper (32) via their respective transport lines (34), (35) and (36). The first component is also pumped through line (38) into the primary hopper (32) using a feed pump (37).

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The modified emulsion and the sensitizing agents are combined using a ribbon blender (39) to produce a sensitized emulsion, which is transported from the ribbon blender (39) via a line (40) using an unloading pump (41). The sensitized emulsion is pumped through a line (42) into the sensitized emulsion storage tank (44). Samples of the sensitized emulsion may be collected using a sample port (43). The complementary reactant, the amine compound, is unloaded and weighed using scales (45) before being loaded into the complementary reactant storage tank (46). When the packaged thickened emulsion explosive is produced, the sensitized emulsion is pumped into the flow line (51) using a feed pump (50). The complementary reactant is pumped through line (47) using feed pump (48) before being centre line injected into the flow line (51) using an injector (49). The modified emulsion and complementary reactant in the flow line (51) are then combined using static mixers (52) to produce the thickened emulsion explosive. The thickened emulsion explosive is transported via a line (53) into the packaging machine (54). The packaged thickened emulsion explosive is then transported using conveyor belts (55) and (56) to the boxing station (57) where it is prepared for transportation.

The second aspect of the present invention and related embodiments are based on the selection of suitable amine compounds that will form an emulsion explosive when mixed with the aqueous oxidizer phase and a fuel phase. That is, in certain embodiments the amine compound functions as an emulsifier, thereby removing the need to use a separate (conventional) emulsifier to form an emulsion of the aqueous and fuel phases. Furthermore, suitable amine compounds are ones that will react with suitable α,β -unsaturated carbonyl compounds to give a desirable rheological effect thereby producing a thickened emulsion explosive comprising the aqueous oxidizer phase and the fuel phase components. Embodiments in accordance with the second aspect of the invention require the addition of appropriate amine compounds to the aqueous oxidizer phase and a fuel phase in a suitable manner and in sufficient amounts to achieve the desired emulsifying effect to form an emulsion explosive. Furthermore, these embodiments then require the addition of an appropriate α,β -unsaturated carbonyl compounds to the emulsion explosive in a suitable manner and in sufficient amounts to achieve a desired thickening effect by reaction in the emulsion of the amine compound and α,β -unsaturated carbonyl compound.

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Thus, the second aspect of the present invention provides a method of forming an emulsion explosive followed by thickening of the emulsion explosive.

As discussed in relation to the first aspect of the present invention, the degree of thickening that is achieved will depend upon a variety of factors including the selection of the α,β -unsaturated carbonyl compound and the amine compound, the relative proportions of the α,β -unsaturated carbonyl compound and the amine compound to each other and to the other components of the emulsion explosive, and the extent to which the amine and α,β -unsaturated carbonyl compounds are dispersed in the aqueous oxidizer phase and the fuel phase. These parameters may be varied in order to control the degree of rheological change that takes place in accordance with the second aspect of the present invention. These parameters will also influence the degree of emulsification that occurs.

In relation to the second aspect, it is believed that the amine compound and the α,β -unsaturated carbonyl compound react by a Michael-type addition reaction, as discussed above in relation to the first aspect of the present invention, to form a crosslinked polymeric network in the finished emulsion explosive. The considerations relating selection of the reactants for the first aspect apply equally to embodiments in accordance with the second aspect. The same exemplary reactants as the first aspect may be useful in the second aspect of the invention.

Without wishing to be bound by theory, it is believed that the formation of a crosslinked polymeric network, which results in thickening of the emulsion explosive, also assists in achieving stable emulsification. This may be because the network in some way binds or interacts with molecules of the fuel phase thereby limiting mobility of such molecules. The limited mobility of the fuel phase molecules is believed to assist in maintaining the dispersion of the aqueous oxidizer phase and accordingly the formation of an emulsion. The amine compound may be used in conjunction with a conventional emulsifier for production of the emulsion explosive. However, emulsification will typically be performed without conventional emulsifiers.

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In this second aspect of the invention the emulsion explosive may be formed by (vigorous) mixing of known fuel phase and oxidiser phase combinations with one or more appropriate amine compounds. The emulsion is formed using the amine compound as emulsifier, with the complementary reactant, i.e. the α,β -unsaturated carbonyl compound, being mixed into the emulsion explosive when thickening is required. Addition of the α,β -unsaturated carbonyl compound may also refine the structure of the emulsion formed using the amine compound alone. For successful implementation of this second aspect of the present invention it is desirable to produce an emulsion using a suitable amine compound, the emulsion having the desired structure of the continuous and discontinuous phases prior the addition of the complementary reactant. The emulsion formed using the amine should be intact when the complementary reactant is added and mixed into the emulsion. The stability of the emulsion formed using the amine will therefore influence how the second aspect of the invention is implemented.

The bulkiness, molecular weight, degree of branching, number of functional groups and/or concentration of the amine compound may influence the viscosity characteristics of the emulsion explosive that is formed and its stability. Amine compounds with two or more terminal functional groups have been found to be particularly useful as emulsifiers in practice of the invention. Useful multi-functional amine compounds are generally polymeric with polar, hydrophilic head groups connected to lipophilic hydrocarbon segments. These polymeric amine compounds have sufficient conformational freedom and flexibility for each amine terminal (head) group to interact with the aqueous phase of the emulsion and for the lipophilic segments to interact with the fuel phase. The effect of these interactions is to stabilise the droplets of the discontinuous phase in the continuous phase and to limit or prevent coalescence of the droplets. For example, amine-terminated butadiene-acrylonitrile copolymers, as described above, have been found useful.

If the molecular weight of the amine compound is too high, the viscosity of the emulsion explosive may increase significantly and blending in the α,β -unsaturated carbonyl and further processing may become difficult. Thus, the selection of an amine compound with relevant functionality and an appropriate molecular weight is particularly important when the amine compound is selected to act as an emulsifier.

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The amine compound may be blended with the fuel component prior to formation of the emulsion explosive, or it may be added externally after a precursor emulsion comprising the aqueous oxidiser and fuel phases has been formed. In the latter case it is likely that the amine compound will migrate to the fuel phase. The precursor emulsion may be an oil-in-water emulsion, but this aspect of the invention may have greater applicability in relation to water-in-oil emulsions.

As in the case of the thickened emulsion explosive of the first aspect, the thickened emulsion explosive may be sensitized or gassed using conventional methods. Substances or mixtures of substances which are oxygen releasing salts or which are themselves suitable as explosive materials may also be added. In addition, the thickened emulsion explosive may be a gassed product and/or the density of the product may be varied as appropriate using known techniques.

For successful implementation of the second aspect of the present invention it is believed to be important that the amine compound is thoroughly dispersed in the emulsion explosive prior to addition of the α,β -unsaturated carbonyl compound. Thorough dispersion of the amine compound will generally occur during formation of the emulsion explosive. The amine and α,β -unsaturated carbonyl compounds may constitute a relatively small proportion of the emulsion explosive and effective mixing may be very important to ensure that the reaction takes place throughout the explosive. The appropriate degree of mixing may be achieved through the use of in-line static mixers.

The α,β -unsaturated carbonyl compound is added to the emulsion when the thickening effect is required to take place. At that time it is believed to be important that the α,β -unsaturated carbonyl compound is mixed thoroughly into the emulsion so that reaction between the amine and α,β -unsaturated compounds takes place throughout the emulsion. In this way localised thickening can be avoided.

In order to enhance the ease with which the α,β -unsaturated carbonyl compound is dispersed in the emulsion explosive it may be desirable to dissolve or disperse the reactant

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into a suitable solvent, which may comprise the fuel as the fuel component, or materials compatible with the fuel component, for example corn oil. The α,β -unsaturated carbonyl compound may be combined with the solvent in a 50/50 ratio determined by weight.

The relative proportions of the amine or α,β -unsaturated carbonyl compounds are generally the same as those for the first aspect of the invention. Similarly, to the first aspect the total weight of amine and α,β -unsaturated carbonyl compounds to be included in the emulsion explosive composition will be 0.4-2.5% based on the total weight of the emulsion explosive composition. Adding the amine compound at a proportion of around 1% based upon the total weight has been found useful when the amine compound acts as the emulsifying agent.

The thickened emulsion explosives in accordance with the second aspect may be utilised for the same applications as those in accordance with the first aspect. The thickening reaction and the resulting thickened emulsion explosive tend to have similar characteristics across all aspects of the invention.

A thickened emulsion explosive in accordance with the second aspect of the invention may be used as a bulk product. In this case, one loading hose may be used to deliver a emulsion explosive formed using the amine compound into the borehole with a separate loading hose delivering the α,β -unsaturated carbonyl compound. Mixing of the α,β -unsaturated carbonyl compound and the emulsion explosive as they exit the respective loading hoses may be achieved using a suitable mixing nozzle. In one embodiment the loading hoses may be arranged in parallel along a common axis. In a preferred arrangement one component may be delivered down a loading hose provided as a centre-line within another larger diameter hose, i.e. as a concentric arrangement. In each case a nozzle mixer may be used to thoroughly blend the components as they exit respective loading hoses.

Figure 1 may also be useful in illustrating implementation of the second aspect of the invention. In an embodiment, an emulsion explosive which comprises as emulsifier an amine compound, an amine-terminated butadiene-acrylonitrile copolymer, is pumped from bulk emulsion storage tank (11) using a pump (12) and into the loading hose (10). While

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in the storage tank (11) the emulsion explosive may be agitated to prevent the phases from separating. The complementary reactant, the α,β -unsaturated carbonyl compound (e.g. epoxidized soy oil acrylate), is centre line injected using pump (13) through the complementary reactant line (14) into the loading hose. As the α,β -unsaturated carbonyl compound is pumped towards the nozzle (15) of the loading hose (10) it passes through a water ring injector (16). A static mixer (17) is positioned at the nozzle (15) and mixes the emulsion explosive and α,β -unsaturated carbonyl compound together to form the thickened emulsion explosive.

The amine compound used to form the emulsion explosive should result in a stable (intact) emulsion. Otherwise, the phases of the emulsion may separate in the borehole. Once in the borehole the reactants will react thereby thickening the emulsion explosive. Thus, in accordance with this aspect of the invention it is possible to load the borehole with an emulsion explosive, which will continue to thicken once it is in the borehole.

Alternatively, it is possible to produce a packaged thickened emulsion explosive by producing an emulsion explosive using the amine as emulsifier, which may also be sensitized. At the packaging facility the emulsion explosive and α,β -unsaturated carbonyl compound are combined to form a thickened product which is then packaged.

The thickened emulsion explosive may be packaged to the desired diameter after the majority of the thickening has occurred. Alternatively, the emulsion explosive composition may be packaged as the emulsion thickens. If a significant proportion of any reaction between the amine compound and the α,β -unsaturated carbonyl compound takes place during packaging, infrastructure costs may be reduced by removing the need to use a cooling bath. However, depending upon the relative stability of the emulsion explosive, in some embodiments it may be desirable for the majority reaction between the reactants, and accordingly the thickening, to occur after packaging.

In some embodiments, it may be desirable to pump the emulsion explosive composition to be packaged into the cartridge production unit using a nozzle similar to the one described above for forming a thickened bulk product. Accordingly, it is possible to prepare the

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product so that the reactants come into contact with each other as the product is being packaged. Mixing may be achieved using a nozzle mixer at the end of the emulsion explosive loading hose. Thus, the components are blended as they exit the loading hose.

The process illustrated in Figure 2, may be modified to produce a product in accordance with the method previously described for the second aspect of the invention. In such an embodiment, an emulsion explosive which comprises a preferred amine compound, an amine-terminated butadiene-acrylonitrile copolymer, is pumped from a bulk emulsion storage tank (18) using a pump (not shown) and into the emulsion line (20) before proceeding as described above to produce the packaged thickened emulsion explosive.

Figure 3 illustrates a process flow diagram of a packaging plant which may be modified so it is suitable for use in accordance with the method previously described for the second aspect of the invention. In such an embodiment, the emulsion explosive may be produced onsite rather than at a separate production plant. Accordingly, the production plant transport truck (26) would be replaced by amine compound, fuel phase component and oxidizer phase component storage tanks and blenders suitable for producing the emulsion explosive.

The emulsion explosive may be sensitized in the same manner as described above. However, the sensitized emulsion explosive may require agitation in the sensitized emulsion storage tank (44) to prevent phase separation. The remainder of the manufacturing process may be performed as described above in relation to the aspect related to the first aspect of the present invention.

In addition to the first and second aspects of the present invention, it may be possible to select suitable amine and α,β -unsaturated carbonyl compounds that will form a thickened emulsion explosive when these compounds are added to and mixed with an aqueous oxidizer phase and a fuel phase. In this case the thickened emulsion may be formed in a single step by mixing of the various components.

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In a further embodiment, a precursor emulsion may be formed using a conventional emulsifier or amine emulsifier as discussed herein. This precursor emulsion may be formed by (vigorous) mixing of known fuel phase and oxidiser phase combinations with the emulsifier(s). However, the precursor emulsion is not stable until the addition of and blending with the reactive amine and α,β -unsaturated carbonyl compounds to produce a thickened emulsion explosive.

Thus precursor emulsion may be formed so as to include either the amine compound or α,β -unsaturated carbonyl compound, with the complementary reactant, i.e. the α,β -unsaturated carbonyl compound or amine, being mixed into the precursor emulsion when thickening is required. Formation of the precursor emulsion with the amine compound or α,β -unsaturated carbonyl compound may result in increased emulsion stability.

In this case, the amine or α,β -unsaturated carbonyl compound may be blended with the fuel component prior to formation of the precursor emulsion, or it may be added externally after the precursor emulsion has been formed. In the latter case it is likely that the reactant compound will migrate to the fuel phase. The precursor emulsion may be an oil-in-water emulsion, but this aspect of the invention may have greater applicability in relation to water-in-oil emulsions. In some embodiments, the α,β -unsaturated carbonyl compound will be the reactant that is added to the fuel phase or externally to the precursor emulsion, with the amine being blended into the precursor emulsion subsequently.

As in the case of the thickened emulsion explosive of the first and second aspects, the thickened emulsion explosive may be sensitized or gassed using conventional methods.

For successful implementation of this aspect of the present invention it is believed to be important that the relevant reactant is thoroughly dispersed in the precursor emulsion prior to addition of the complementary reactant. As in other aspects, the amine and α,β -unsaturated carbonyl compounds may constitute a relatively small proportion of the emulsion explosive and effective mixing may be very important to ensure that the reaction takes place throughout the explosive.

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The addition of the amine or α,β -unsaturated carbonyl compound to the relevant component of the precursor emulsion, or the precursor emulsion itself, (and thorough blending therewith) preferably does not cause any significant viscosity increase in itself. Any viscosity change should not make subsequent handling and processing unduly difficult.

The complementary reactant is added to precursor emulsion the when the emulsifying and thickening effects are required to take place. At that time it is believed to be important that the complementary reactant is mixed thoroughly into the precursor emulsion so that reaction between the amine and α,β -unsaturated compounds takes place throughout the precursor emulsion. In this way localised thickening and/or emulsification can be avoided.

In these alternative embodiments the relative and gross proportions of the amine or α,β -unsaturated carbonyl compounds are generally the same as those for the first aspect of the invention.

The thickened emulsion explosives in accordance with these alternative embodiments may be utilised for the same applications as those in accordance with the first and second aspects. The thickening reaction and the resulting thickened emulsion explosive tend to have similar characteristics across all aspects of the invention.

Thus, a thickened emulsion explosive in accordance with these alternative embodiments may be used as a bulk product. In this case, one loading hose may be used to deliver a emulsion explosive containing the amine compound into the borehole with a separate loading hose delivering the α,β -unsaturated carbonyl compound. Alternatively, the fuel phase component and the relevant reactant may be delivered using one hose and the aqueous oxidizer phase and the complementary component may be delivered in the other. Mixing of these individual components as they exit the respective loading hoses may be achieved using a suitable mixing nozzle. In one embodiment the loading hoses may be arranged in parallel along a common axis or, preferably, a concentric arrangement.

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Depending upon the relative stability of the precursor emulsion, it may be desirable for the amine and α,β -unsaturated carbonyl compounds to react such that emulsification of the precursor emulsion occurs during mixing and as it is being pumped into the borehole. Otherwise, the phases of the precursor emulsion may separate in the borehole. Ideally, the precursor emulsion will be emulsified to form an emulsion explosive as the reactants react and as it is pumped into the borehole. Once in the borehole the reactants will continue to react thereby thickening the emulsion explosive. Thus, in accordance with this aspect of the invention it is possible to load the borehole with an emulsion explosive, which will continue to thicken once it is in the borehole.

Alternatively, it is possible to produce a packaged thickened emulsion explosive by producing the precursor emulsion, which may also be sensitized. At the packaging facility the precursor emulsion and complementary reactant are combined to form an emulsified and thickened product which is then packaged.

As discussed previously, the base emulsion or precursor emulsion used in accordance with all aspects of the present invention include the known fuel phase and oxidiser phase combinations for the production of conventional emulsion explosives. For convenience, unless otherwise stated, in the description below the term "emulsion" is taken to include a precursor emulsion.

Suitable oxygen releasing salts for use in the oxidizer phase of the emulsion of the present invention include the alkali and alkaline earth metal nitrates, chlorates and perchlorates, ammonium nitrate, ammonium chlorate, ammonium perchlorate and mixtures thereof. The preferred oxygen releasing salts include ammonium nitrate, sodium nitrate and calcium nitrate. However, the effect of calcium nitrate upon the rate of thickening should be considered when selecting salts. The oxygen releasing salt typically comprises ammonium nitrate or a mixture of ammonium nitrate and sodium nitrate.

If the emulsion is a water-in-oil emulsion, typically the oxygen releasing salt component of the oxidizer phase of the compositions of the present invention generally comprises from 45 to 95 % w/w and preferably from 60 to 90 % w/w of the total thickened emulsion

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explosive. In compositions wherein the oxidizer phase comprises a mixture of ammonium nitrate and sodium nitrate the preferred composition range for such a blend is from 5 to 80 parts of sodium nitrate for every 100 parts of ammonium nitrate.

Therefore, in the preferred thickened emulsion explosive the oxygen releasing salt component of the oxidizer phase comprises from 45 to 95 % w/w (of the total thickened emulsion explosive) ammonium nitrate or mixtures of from 0 to 40 % w/w, sodium or calcium nitrates and from 50 to 95 % w/w ammonium nitrate.

Typically the amount of water employed in the oxidizer phase of the thickened emulsion explosives of the present invention is in the range of from 0 to 30 % w/w of the total emulsion composition. Preferably the amount employed is from 4 to 25 % w/w and more preferably from 6 to 20 % w/w.

Suitable organic fuels for use in the fuel phase include aliphatic, alicyclic and aromatic compounds and mixtures thereof which are in the liquid state at the formulation temperature. Suitable organic fuels may be chosen from fuel oil, diesel oil, distillate, furnace oil, kerosene, naphtha, paraffin oils, benzene, toluene, xylenes, asphaltic materials, polymeric oils such as the low molecular weight polymers of olefines, animal oils, vegetable oils, fish oils and other mineral, hydrocarbon or fatty oils and mixtures thereof. Preferred organic fuels are liquid hydrocarbons generally referred to as petroleum distillates such as gasoline, kerosene, fuel oils and paraffin oils. Typically, the fuel phase of the emulsion comprises from 2 to 15 % w/w and preferably 3 to 10 % w/w of the total thickened emulsion explosive.

As discussed above, all aspects of the present may involve the use of conventional emulsifiers. The emulsifier may be chosen from the wide range of emulsifiers known in the art for the preparation of emulsion explosives. The emulsifier used may be one of the well known emulsifiers based on the reaction products of poly[alk(en)yl] succinic anhydrides and alkylamines, including the polyisobutylene succinic anhydride (PiBSA) derivatives of alkanolamines. Other suitable emulsifiers for use in the thickened emulsion explosive of the present invention include alcohol alkoxylates phenol 5 alkoxylates,

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poly(olyalkylene)glycols, poly(oxyalkylene)fatty acid esters, amine alkoxylates, fatty acid esters of sorbitol and glycerol, fatty acid salts, sorbitan esters, poly(oxyalkylene) sorbitan esters, fatty amine alkoxylates, poly(oxyalkylene)glycol esters, fatty acid amines, fatty acid amide alkoxylates, fatty amines, quaternary amines, alkyloxazolines, alkenyloxazolines, imidazolines, alkylsulphonates, alkylarylsulphonates, alkylsulphosuccinates, alkylarylsulphonates, alkylsulphosuccinates, alkylphosphates, alkenylphosphates, phosphate esters, lecithin, copolymers of poly(oxyalkylene)glycols and poly(12-hydroxystearic)acid and mixtures thereof.

Typically, the emulsifier of the emulsion comprises up to 5 % w/w of the thickened emulsion explosive. Stable emulsions can be formed using relatively low levels of emulsifier and for reasons of economy it is preferable to keep the amount of emulsifying agent used to the minimum required to form the emulsion. The preferred level of emulsifying agent used is in the range of from 0.1 to 3.0 % w/w of the thickened emulsion explosive. However, lower levels of emulsifier may be used in certain embodiments. Alternatively or additionally, in the second aspect, the amine compound functions as an emulsifier.

If desired, other optional fuel materials, hereinafter referred to as secondary fuels may be incorporated into the emulsion in addition to the fuel phase. Examples of such secondary fuels include finely divided solids and water miscible organic liquids which can be used to partially replace water as a solvent for the oxygen releasing salts or to extend the aqueous solvent for the oxygen releasing salts in the oxidizer phase. Examples of finely divided materials include sulphur, aluminium, urea and carbonaceous materials such as gilsonite, comminuted coke or charcoal, carbon black, resin acids such as abietic acid, sugars such as glucose or dextrose and vegetable products such as starch, nut meal, grain meal and wood pulp. Examples of water miscible organic liquids include alcohols such as methanol, glycols such as ethylene glycol, amides such as formamide and urea and amines such as methylamine. Typically the optional secondary fuel component of the composition of the present invention comprises up to 30 % w/w of the total composition.

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It lies within the invention that there may also be incorporated into the emulsion explosive (prior to thickening) other substances or mixtures of substances which are oxygen releasing salts or which are themselves suitable as explosive materials. These include doping the emulsion with ammonium nitrate prills of low density or high density, sodium nitrate prills, calcium nitrate prills, sodium perchlorate prills and/or any known oxidizers in prill form, including those mixed with diesel oil and/or nitroalkane, for example, nitrotoluene etc; doping the emulsion with RDX, PETN, TNT, MAN, EAN, EDDN or HN as organic nitrate sensitizer; and doping the emulsion with granulated aluminum powder, atomized aluminum, paint grade aluminum, foamed aluminum, nanoparticle aluminum, foam nickel, foamed iron, foamed silicon, foamed aluminum silicon alloy metal etc.

The base emulsion or the modified emulsion may be sensitized using foamed metal, foams of natural or synthetic liquids or solids, foams of ammonium nitrate or oxygen releasing salts, water based foams, or oil based foam etc. Additionally or alternatively, metal based nano-materials, natural or synthetic nano-materials, or inorganic or organic nano-materials based upon amine nitrate, etc. may be used. Furthermore, the base emulsion or modified emulsion may be sensitized by gassing. Gassing may be performed using a number of compounds including nitrite compounds, organic carbonates, inorganic carbonates, peroxides, and nitrogen gas generating from an inorganic or organic compound.

The invention is now illustrated further by, but is in no way limited to, the following examples.

Examples

Throughout these examples the following abbreviations or acronyms are used:

ATBN	amine terminated polybutadiene acrylonitrile - Hycar 1300X21 polymer
ESOA	epoxidized soybean oil acrylate
AN	ammonium nitrate
SN	sodium nitrate
CN	calcium nitrate

SMO	sorbitan monooleate
SSO	sorbitan sesquiolate
DN60	polyisobutylene succinic anhydride derivative with diethanol amine from Nelson Brothers
DN80	polyisobutylene succinic anhydride derivative with diethylethanol amine from Nelson Brothers
HT-22	Paraflex™, highly purified mineral oil from PetroCanada
LZ2824S	polyisobutylene succinic anhydride derivative with diethanol amine from Lubrizol™
SG1100	SoyGold 1100, fatty acid methyl ester of soya bean oil, from Ag Environmental Products L.L.C
VoD	Velocity of Detonation (m.s^{-1})

Laboratory Synthesis of the Thickened emulsion explosive

Example 1

Table 1

Ingredient	Proportion %w/w	Mass (g)
ATBN	0.49%	10.0g
Mineral oil	7.46%	150.0g
AN	75.03%	1508.8g
Water	16.47%	331.2g
ESOA	0.55%	11.0g

The composition of the sample is shown in Table 1 and produced as follows. The amine compound, ATBN, was mixed into the mineral oil in a Hobart bowl at mixing at speed 2. The ammonium nitrate solution was produced by dissolving the ammonium nitrate in the

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water. The ammonium nitrate solution was then slowly poured into the mixing bowl while the mixer is running. The mixture was then digested for 2 minutes and continuously mixed for another 3 minutes. The resulting precursor emulsion was very fluid, globular and unstable with a viscosity of 6000 cps at 75°C when measured using a Brookfield Viscometer using spindle 7 at 20rpm. The α,β -unsaturated carbonyl compound, ESOA, was mixed into the emulsion at speed 2 for 11 minutes. The resulting emulsion was stable, thick and gelled with a Brookfield viscosity at 75°C as shown in Table 2.

Table 2

Spindle	Speed (rpm)	Brookfield Viscosity (cps)
7	10	123000
7	20	90000
T bar E	5	240000
T bar E	10	170000
T bar E	20	110000
T bar E	50	46750
T bar E	100	29000

Example 2

Table 3

Ingredient	Proportion %w/w	Mass (g)
DN60	1.24%	24.8g
SMO	0.17%	3.4g
HT-22	2.32%	46.4g
Corn oil	0.72%	14.4g
ESOA	1.24%	24.8g
AN/SN/Water (77/11/12)	90.73%	1814.6g
K20 glass microballoons	2.86%	57.2g
ATBN	0.72%	14.4g

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In this example, a further composition was synthesized by weighing the required DN60, SMO, HT-22 and ESOA (shown in Table 3) into the Hobart mixing bowl, applying steam to the mixing bowl and mixing the components at speed 2. When the temperature of the oil mixtures reached 60 °C, the AN/SN/Water solution was poured into the oil mixture. It took 2 minutes to digest the solution to form the water in oil emulsion. The solution was then mixed further at speed 2 for 3 minutes. Then the Brookfield viscosity was taken.

Brookfield viscosity – Spindle 7 at 10 rpm at 82 °C=88400 cps
 Spindle 7 at 20 rpm at 82 °C=43800 cps

The Hobart bowl was placed back to the mixer and mixed further at speed 3 for 3 minutes to refine the emulsion, before the Brookfield viscosity was measured again.

Brookfield viscosity – Spindle 7 at 10 rpm at 76 °C=250000 cps
 Spindle 7 at 20 rpm at 76 °C=135000 cps

Then K20 glass microballoons were added and mixed while the steam was still running through the bowl. The Brookfield viscosity was then measured.

Brookfield viscosity – Spindle 7 at 10 rpm at 76 °C=275000 cps
 Spindle 7 at 20 rpm at 76 °C=157000 cps

The ATBN was mixed with corn oil and then mixed into the emulsion. The emulsion gelled and became thick.

After 2 months storage at room temperature, a 25 mm diameter cartridge of the resulting thickened emulsion explosive at a density of 1.17 g/cc was shot with an electric blasting detonator. The velocity of detonation was measured using the point to point target wire method as 4504 m/sec.

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Example 3

Table 4

Ingredient	Proportion %w/w	Mass (g)
DN60	1.493%	29.86g
SMO	0.207%	4.14g
HT-22	2.810%	56.2g
ESOA	0.70%	14.0g
AN/SN/Water solution (77/11/12)	94.79%	1895.8g

The required amount of DN60, SMO, HT-22 and ESOA, as shown in Table 4, was weighed into a Hobart mixing bowl, steam was applied to the mixing bowl and the components were mixed at speed 2. When the temperature of the oil mixture reached 60 °C, the AN/SN/Water solution was poured into the oil mixture. The resulting mixture was then digested for 1 minutes and 30 seconds to form the water-in-oil emulsion. The emulsion was then mixed further at speed 2 for 3 minutes and 30 seconds. The Brookfield viscosity was then taken.

Brookfield viscosity – Spindle 7 at 10 rpm at 84 °C=72800 cps
 Spindle 7 at 20 rpm at 84 °C=38000 cps

The Hobart bowl was placed back into the mixer and mixed further at speed 3 for 3 minutes to refine the emulsion. Then the Brookfield viscosity was taken.

Brookfield viscosity – Spindle 7 at 10 rpm at 71 °C=220000 cps
 Spindle 7 at 20 rpm at 71 °C=114000 cps

T bar E at 10 rpm at 71 °C=140000 cps

Then 7.5 g of ATBN, mixed with 7.5 g of corn oil, was added and mixed into to 1000.0 g of the sample emulsion. The Brookfield viscosity was then taken.

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Brookfield viscosity (time at zero) - T bar E at 10 rpm at 71 °C=185000 cps
 (after 30 minutes) T bar E at 10 rpm at 71 °C=215000 cps
 (after 4 hours) T bar E at 10 rpm at 71 °C=310000 cps

Example 4

Table 5

Ingredient	Proportion %w/w	Mass (g)
LZ2824S	0.636%	15.90g
Diesel Oil	2.542%	63.55g
SMO	0.497%	12.43g
AN	76.544%	1913.60g
Water	16.802%	420.05g
K-20 glass microballoons	2.979%	74.48g

The required amount of LZ2824S, SMO, Diesel Oil, as shown in Table 5, was weighed into a Hobart mixing bowl, the steam was applied to the mixing bowl and the mixture was mixed at speed 2. The AN and the water were mixed together to produce a solution. When the temperature of the oil mixtures reached 50°C, the AN/Water oxidizer solution was poured into the oil mixture. The mixture was digested for 1 minute and 15 seconds to form a water-in-oil emulsion. The emulsion was mixed further at speed 2 for 4 minutes. Then the Brookfield viscosity was taken.

Brookfield viscosity – Spindle 7 at 10 rpm at 78 °C=31500 cps
 Spindle 7 at 20 rpm at 78 °C=17000 cps

The Hobart bowl was placed back to the mixer and mixed further at speed 3 for 3 minutes to refine the emulsion. Then the Brookfield viscosity was taken.

Brookfield viscosity – Spindle 7 at 10 rpm at 70 °C=80000 cps
 Spindle 7 at 20 rpm at 70 °C=41500 cps

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Then K-20 glass microballoons were added and mixed into the emulsion while the steam was still running through the bowl.

A 2000g sample of the emulsion was divided into two equal parts. The following materials were added into the emulsion and mixed at a temperature of between 70-75 °C.

	<u>Sample 1</u>	<u>Sample 2</u>
ESOA	2.02g	2.02g
SG1100	3.25g	3.25g
Corn Oil	3.25g	3.25g

The viscosity of sample 1 and sample 2 dropped slightly due to the additional oil added into the emulsion. The following materials were also added to the samples.

	<u>Sample 1</u>	<u>Sample 2</u>
ATBN	3.50g	3.50g
LZ2824S	0.70g	0.70g
Diesel Oil	2.80g	2.80g
Calcium Nitrate (40%)	0.00g	10.0g

The ATBN was mixed into the emulsion resulting in the emulsion thickening and gelling in less than one minute. The samples were packaged into 25 mm diameter High Density Polyethylene (HDPE) film for compression tests. The samples had a length of 30mm and were stored at room temperature prior to performing the compression tests. The results of the compression tests following 2 days, 4 days and 1 week of storage are shown in Figures 4, 5 and 6, respectively.

Sample 1 and sample 2 test specimens were shot at room temperature with an electric blasting detonator. The results of the shooting tests are shown below in Table 6.

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Table 6

25mm dia AN/W (82/18)	After 1 Day	After 4 Days	After 9 Days	After 2 month, 17°C shooting temperature
Sample 1	VoD: 5427 Density: 1.118	VoD: 5000 Density: 1.128	VoD: 4961 Density: 1.133	VoD: 4433 Density: 1.120
Sample 2	VoD: 5163 Density: 1.101	VoD: 4739 Density: 1.119	VoD: 4774 Density: 1.123	VoD: 4550 Density: 1.122

Point to point VoD measurement of 63.5mm (2.5")

Example 5

Emulsions were prepared using a standard operating procedure for manufacturing small-scale laboratory mixes. The required amount of an aqueous oxidizer solution at 90°C was added slowly for five minutes to the fuel phase containing ESOA at speed 2 in a steam jacketed mixing bowl. Additional emulsion refinement was required for the packaged emulsion formulations and achieved by mixing at speed 3 for 5 minutes. Once the bulk or packaged emulsion was refined to the desired viscosity and droplet size, the product was sensitized with plastic microspheres to the desired density. After the addition of the microspheres ATBN was then added to the emulsion and thoroughly mixed for about two minutes and then cartridged in plastic or cardboard containers.

The formulations used to manufacture the laboratory scale packaged and bulk thickened emulsion explosives are given below.

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Table 7: Bulk and Packaged formulations containing ESOA and ATBN

	Ingredient	Bulk	Packaged
Oxidizer	AN	77.646	72.610
	SN	0.000	10.370
	Water	17.044	11.320
Oil Phase	DN80	0.645	0.000
	Diesel Oil	2.597	0.000
	SMO	0.504	0.000
	Corn Oil	0.640	0.326
	LZ2824S	0.000	2.490
	SSO	0.000	0.510
	HT-22	0.000	1.104
	ESOA	0.199	0.200
Sensitizer	Microspheres	0.000	0.300
Other	DN80	0.074	0.000
	Diesel oil	0.298	0.000
	LZ2824S	0.000	0.311
	SSO	0.000	0.072
	ATBN	0.372	0.375

*Determining the Optimum Level of ESOA and ATBN***Example 8**

Experimental laboratory batches of packaged and bulk emulsions were evaluated to determine the optimum level of ESOA and ATBN required to produce a cost effective and high quality thickened emulsion explosive compositions. The following table shows the process of reducing ESOA and ATBN to optimum levels. Thickened emulsion explosive samples with a nonfluid, deformable rheology are said to have polymerized.

Table 8: Optimum Level of ESOA and ATBN in Polymerized Emulsions

Matrix	% w/w ESOA	% w/w ATBN	Temp (°C)	Viscosity using T bar (10 ³ cps) at 5 rpm	Compression force after 1 day	Comments
Bulk	1.3	0.175	75	30	60	Product did not polymerize
Bulk	1.3	0.25	75	32.4	70	Gelled, poor plasticity
Bulk	1.3	0.375	75	50	85	Polymerization after 3 days
Packaged	1.3	0.75	75	342	210	Polymerized after 1 day
Bulk	1.3	0.5	75	53.8	100	Polymerization after 2 days
Packaged	1.3	0.375	75	213	150	Polymerized after 2 days
Packaged	1.3	0.25	75	200	145	Does not polymerize
Bulk	0.9	0.375	75	44	80	Polymerization after 4 days
Bulk	0.9	0.31	75	53	130	Fair plasticity
Bulk	0.5	0.25	75	38	75	Fair plasticity
Bulk	0.2	0.375	75	47	85	Good elasticity and polymerization after 3 days
Bulk	0.2	0.25	75	53	175	Product did not polymerize

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The optimum level of ESOA and ATBN was found to be 0.2% and 0.375%, respectively. At 0.375% ATBN in the product, an acceptable rate of polymerization was achieved. Any level below 0.375% did not polymerize.

Tests of pure ESOA and ATBN indicated that a 30/70 blend gave the quickest rate of polymerization. Therefore, the amount of ESOA selected was 0.2%. This is a 35:65 ratio of ESOA to ATBN. Higher ratios of ATBN will polymerize faster when the chemicals are combined as neat reactants. However, when mixed into a large volume matrix, there must be enough ESOA to disperse and polymerize with the ATBN. For this reason, nothing below 0.2% was tested.

Use of only ATBN in the emulsion without the α,β -unsaturated carbonyl compound, ESOA, caused it to thicken but with no plasticity. Emulsions containing only ESOA but no polymer will not gel or thicken in storage.

Oil used for Cleaning Process Equipment

Example 9

To determine how to clean the plant equipment after producing the thickened emulsion explosive, a solvent must be found that dissolves the product. Several oils were used experimentally to find the best solvent. In each test a mixture comprising 95.18% the contemplated oil, 2.41% ESOA and 2.41% ATBN was mixed and observed. The oils considered were: SG1100, SC1500 (biodegradable methyl esters derived from soybean oil), CE110 (biodegradable methyl ester derived from canola oil), Varsol 110, HT-22, Corn Oil, and Diesel oil.

The solubility of the mixture was determined visually in the laboratory. The SG1100 was the best solvent for the ESOA and ATBN product, and may be used for cleaning plant equipment. HT-22, corn oil, and diesel oil did not completely dissolve the product.

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Emulsion Pilot Plant Trials

Example 10

The purpose of the Emulsion Pilot Plant Trials was to determine the feasibility of manufacturing thickened emulsion explosives in a non-laboratory setting.

Approximately one tonne of an explosive emulsion composition containing a carbonaceous fuel continuous phase, an aqueous discontinuous phase containing dissolved oxidiser salt and an emulsifier was produced in the EMMA II pilot plant using pin mill mixer technology. ESOA was mixed into the matrix using a 125L Panocopter kitchen mixer. ATBN was delivered at the centre of the emulsion to obtain uniform mixing. A blue dye was added to the ATBN to help determine the dispersion within the matrix as it was mixed and to assist evaluating the amount of mixing.

The experiments were carried out using a 5m loading hose. All the flows were calibrated and curves were established. The emulsion matrix containing ESOA was pumped at a rate of 30 kg/min with 2.0% water lubrication. The addition of ATBN was delivered at 2.0% using the F5 method, in the centre of the emulsion. Two Sulzer static mixers were installed at the end of the loading hose to obtain uniform mixing with ATBN additive. The emulsion pumping pressure at a flow rate of 30kg/min was measured as 11 bars and 14 bars of pressure at the ATBN pump.

Two plexiglass tubes (3.5 and 4 inch in diameter) were filled with the thickened emulsion explosive to evaluate up-hole retention properties. The thickened emulsion explosive stayed within the clear plexiglass tubes without slumping for over three months. Accordingly, the thickened emulsion explosive demonstrated excellent up-hole retention properties.

The gassing performance was also examined to determine if the thickened emulsion explosive could be chemically gassed. The thickened emulsion explosive was capable of being gassed to a cup density of 1.05 g/cc after 45 minutes at 250°C. Results showed that

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the thickened emulsion explosive did not detrimentally affect the chemical gassing process.

The addition of ESOA externally to the matrix did not affect the consistency of the matrix produced. The addition of ESOA internally also did not affect the consistency of the matrix.

When ATBN was added, mixing was found to be a critical part of the product production process. If the emulsion was not mixed thoroughly, the thickening rate reduced.

After the thickening had taken place, it was found that the product caked inside the hopper and it became very difficult to clean. For this reason, it became crucial to find a solvent to dissolve the polymer and clean the plant equipment.

New Concept in Manufacturing Packaged Emulsion

Example 11

In a field trial a bulk manufacturing plant was organized to examine the feasibility manufacturing a packaged thickened emulsion explosive. The matrix formulation is listed below:

Table 9: Formulation for Packaged Thickened emulsion explosive

		Composition	Formulation
Oil Phase	DN60	56.99	2.85
	SSO	12.02	0.601
	HT-22	18.82	0.891
	SG1100	4.61	0.231
	Corn Oil	4.61	0.231
	ESOA	0.40	0.198
Oxidizer	AN	77.00	71.61
	SN	11.00	10.23
	Water	12.00	11.16

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Approximately 5,000 lbs of an emulsion matrix containing 0.2% ESOA in the oil phase was manufactured on the Stir-Pot-Static-Mixer. The matrix viscosity of the base matrix containing ESOA was measured at 82,000 cps with 2 DY static mixers with a manufacturing pressure of 150 psi.

The optimum process parameters in manufacturing packaged emulsion matrix through a Stir-Pot-Static-Mixer emulsifier unit were determined and are summarized in Table 10.

Table 10: Matrix Containing ESOA Manufacturing Process Conditions

Trial run (with ESOA)	5%	7%
AN / SN / water solution tank temp (°C)	93	93.3
AN / SN / water fudge point (°C)	74.8	74.8
AN / SN / water solution flow rate (lb/min)	192.2	185.5
Surfactant / Oil Phase tank temp (°C)	60	60
Surfactant / Oil Phase run temp (°C)	57.7	57.7
Oil phase flow rate (lb/min)	10.2	14.1
Stir pot stirring speed	609	608
Number of mixers	2	2
Type of inline mixer	DY	DY
Transfer pump speed	203	285
Matrix pumping pressure (psi)	150	130
Matrix temperature (°C)	88	88
Matrix viscosity spindle 7 @ 20 rpm (cps)	82000	72000

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*Thickened emulsion explosive Mine Trial***Example 12**

Five 25 kg cases of packaged 25x300mm cartridge packaged thickened emulsion explosive were produced in the laboratory and shipped to a mine test site. The thickened emulsion explosive was evaluated against Magnafrac in an underground up-hole stope. The main purpose of the trial was to determine how the packaged thickened emulsion explosive performed when loading up-holes using a cartridge loader. The loading operation was conducted in the 1330 stope. The up-hole borehole diameter was 54 mm and 13.4 to 18.9 metres in length. In the 54 mm diameter up-holes the thickened emulsion explosive compacted as well as the Magnafrac packaged emulsion. Compaction measured for the Magnafrac product was 92% and the thickened emulsion explosive compacted between 92 and 95%. Very little blow-back was observed when loading either the composition or the Magnafrac product. No product crystallization was observed when loading the thickened emulsion explosive product through the cartridge loader. Overall the trial was a success, which indicates that no foreseeable problems should be encountered when loading the packaged polymerized emulsion with a cartridge loader.

Cartridge Loader Operating Parameters:

25mm cartridge loader.

25mm grooved loading hose 30.5 metres in length.

72 psi operating pressure.

Approximately 1.5 metre standoff from the end of the loading hose to the emulsion

Cup of water used in the cartridge loader when cartridges slowed down in the hose

Trial results:

Loading was conducted in the 1330 up-hole stope. Tests were compared to Magnafrac emulsion cartridges used at the mine. For these tests, 25x300mm diameter emulsion cartridges were used. To ensure the cartridge loader was operating properly and to set the proper operating pressure the back rows were loaded with the Magnafrac product prior to loading the thickened emulsion explosive composition. When the loader was operating

properly, compaction tests were performed on the Magnfrac emulsion and the thickened emulsion explosive composition. Test results are shown in Table 11.

Table 11: Polymerized Compaction Results

Product	Up-hole Diameter	Borehole Length	Weight	Compaction
Magnafrac	54 mm	10.67 meters	25 kg	92.4%
Magnafrac	54 mm	10.67 meters	25 kg	92.4%
Magnafrac	54 mm	9.45 meters	25 kg	104% (broke into adjacent hole)
Thickened Emulsion Explosive	54 mm	10.36 meters	25 kg	95%
Thickened Emulsion Explosive	54 mm	9.75 meters	25 kg	104% (broke into adjacent ring)
Thickened Emulsion Explosive	54 mm	10.67 meters	25 kg	92.4%

Effect of Calcium Nitrate (CN) on Thickening Rate

Example 13

The effect of calcium nitrate on the thickening or polymerization rate was studied as both an external additive and an internal additive to the oxidizer phase. The viscosities and compression results were conducted at 1, 5, and 16-day intervals.

The experimental formulations are given below:

Table 12: Formulations for Effect of CN on Polymerization Rate

	Sample #	1055-57-1	1055-57-2	1055-58-1	1055-58-2	1055-59-1	1055-59-2
Oil Phase	SWOIL DN80						
	DO#2	3.1887	3.1572	3.1887	3.1572	3.1887	3.1572
	SMO	0.4983	0.4933	0.4983	0.4933	0.4983	0.4933
	ESOA	1.2656	1.2531	1.2656	1.2531	1.2656	1.2531
	CORN OIL	0.0000	0.0000	0.6328	0.6266	0.3164	0.3133
	SG1100	0.6328	0.6266	0.0000	0.0000	0.3164	0.3133
Oxidizer	OXIDIZER	93.6701	92.7427	93.6701	92.7427	93.6701	92.7427
Comp B	SWOIL DN80						
	DO#2	0.3722	0.3685	0.3722	0.3685	0.3722	0.3685
	ATBN	0.3722	0.3685	0.3722	0.3685	0.3722	0.3685
External Addition	CN Sol'n (40%)	0.0000	0.9901	0.0000	0.9901	0.0000	0.9901
	TOTAL	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000

Results

- 5 The viscosity for each of the six formulae discussed above was tested at 1, 5, and 16 days, along with the compression data. The following data was taken with the T Bar E using the Brookfield viscometer, at 1 rpm and at room temperature.

Table 13: Results for Effect of Calcium Nitrate on Polymerization Rate

10

Brookfield Viscosity (10^4 cps) using T bar E at 1 rpm measured at room temperature						
Sample #	1055-57-1	1055-57-2	1055-58-1	1055-58-2	1055-59-1	1055-59-2
1 Day	153	200	169	229	153	200
5 Day	340	465	300	OVER	330	OVER
16 Day	414	OVER	298	OVER	330	OVER

This data shows that the addition of CN greatly increases the viscosity both initially, and over time, compared with the omission of CN.

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The compression data was taken at the same intervals, and the results are shown in Figures 7-9.

The results show that the addition of CN into the oxidation phase or externally, will enhance the rate of polymerization and enhance plasticity of the product. Zinc nitrate and Urea did not have any effect on the rate of polymerization.

While calcium nitrate increases the rate of polymerization, it is not recommended for use due to the decreased sensitivity versus AN or SN. Additional microspheres are needed when calcium nitrate is used. Also, adding calcium nitrate increases the cost of production.

Zinc nitrate did not show the same polymerization effect as calcium nitrate, even though it also contains a di-cation (Ca^{+2} and Zn^{+2}). This may be due to the pH difference of Ca^{+2} and Zn^{+2} ions or the chelating property of calcium.

Rate of Polymerization

Example 14

When pure ESOA and ATBN are mixed, they form a polymerized resin. The rate at which the two components polymerized had a direct relationship to the ratio of ESOA to ATBN.

The following percentages of ESOA and ATBN were mixed and the amount of time before polymerization is detected was recorded:

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Table 14: Set Times for Pure ESOA and ATBN

ESOA%	ATBN%	Set Time (minutes)
30	70	35
40	60	45
50	50	60
60	40	120
70	30	240

This data was used to help determine the 0.2/0.375 ratio of ESOA to ATBN used in the formulation.

Embodiments have been described herein with reference to the figures and examples. However, some modifications to the described embodiments and/or examples may be made without departing from the spirit and scope of the described embodiments, as described in the appended claims.

The reference in this specification to any prior publication (or information derived from it), or to any matter which is known, is not, and should not be taken as an acknowledgment or admission or any form of suggestion that that prior publication (or information derived from it) or known matter forms part of the common general knowledge in the field of endeavour to which this specification relates.

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

Claims

1. A method of producing a thickened emulsion explosive, which method comprises reacting in an emulsion explosive an amine compound and an α,β -unsaturated carbonyl compound such that thickening of the emulsion explosive occurs, wherein the α,β -unsaturated carbonyl compound is selected from aldehydes, ketones and acrylates.
5
2. The method according to claim 1, wherein the α,β -unsaturated carbonyl compound is an acrylate.
3. The method according to claim 2, wherein the α,β -unsaturated carbonyl compound is an epoxidized soybean oil acrylate.
10
4. The method according to any one of claims 1 to 3, which method comprises forming the emulsion explosive by mixing an aqueous oxidizer phase, a fuel phase and the amine compound and reacting in the emulsion explosive the amine compound and the α,β -unsaturated carbonyl compound such that thickening of the emulsion explosive occurs.
- 15 5. The method according to any one of claims 1 to 4, wherein the amine compound and α,β -unsaturated carbonyl compound are reacted in a borehole.
6. A thickened emulsion explosive containing a thickening agent comprising a reaction product of an amine compound and an α,β -unsaturated carbonyl compound, wherein the α,β -unsaturated carbonyl compound is selected from aldehydes, ketones and acrylates.
- 20 7. The thickened emulsion explosive according to claim 6, wherein the α,β -unsaturated carbonyl compound is an acrylate.
8. The thickened emulsion explosive according to claim 6 or 7, wherein the α,β -unsaturated carbonyl compound is an epoxidized soybean oil acrylate.
9. A thickened emulsion explosive produced by the method according to any one of
25 claims 1 to 4.

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10. The thickened emulsion explosive according to any one of claims 6 to 9, wherein the thickened emulsion is a packaged emulsion explosive.

11. A method of loading a borehole with a bulk thickened emulsion explosive, which method comprises: introducing an emulsion explosive into the borehole; and reacting in the
5 borehole an amine compound and an α,β -unsaturated carbonyl compound in the emulsion explosive such that thickening of the emulsion explosive occurs, wherein the α,β -unsaturated carbonyl compound is selected from aldehydes, ketones and acrylates.

12. The method according to claim 11, wherein the α,β -unsaturated carbonyl compound is an acrylate.

10 13. The method according to claim 12, wherein the α,β -unsaturated carbonyl compound is an epoxidized soybean oil acrylate.

14. The method according to any one of claims 11 to 13, which method comprises: forming the emulsion explosive by mixing an aqueous oxidizer phase, a fuel phase and the amine compound; introducing the emulsion explosive into the borehole; and reacting in the
15 borehole the amine compound and the α,β -unsaturated carbonyl compound in the emulsion explosive such that thickening of the emulsion explosive occurs.

15. A method of producing a packaged emulsion explosive comprising: reacting in an emulsion explosive an amine compound and an α,β -unsaturated carbonyl compound such that thickening of the emulsion explosive occurs; and packaging the emulsion explosive, wherein
20 the α,β -unsaturated carbonyl compound is selected from aldehydes, ketones and acrylates.

16. The method according to claim 15, wherein the α,β -unsaturated carbonyl compound is an acrylate.

17. The method according to claim 16, wherein the α,β -unsaturated carbonyl compound is an epoxidized soybean oil acrylate.

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18. The method according to any one of claims 15 to 17, which method comprises forming an emulsion explosive by mixing an aqueous oxidizer phase, a fuel phase and the amine compound, and reacting the amine compound and the α,β -unsaturated carbonyl compound in the emulsion explosive such that thickening of the emulsion explosive occurs.

5 19. Use in a blasting operation of a thickened emulsion explosive according to any one of claims 6 to 10.

20. A method of blasting which comprises: loading a borehole with a thickened emulsion explosive according to any one of claims 6 to 10; and detonating the thickened emulsion explosive.

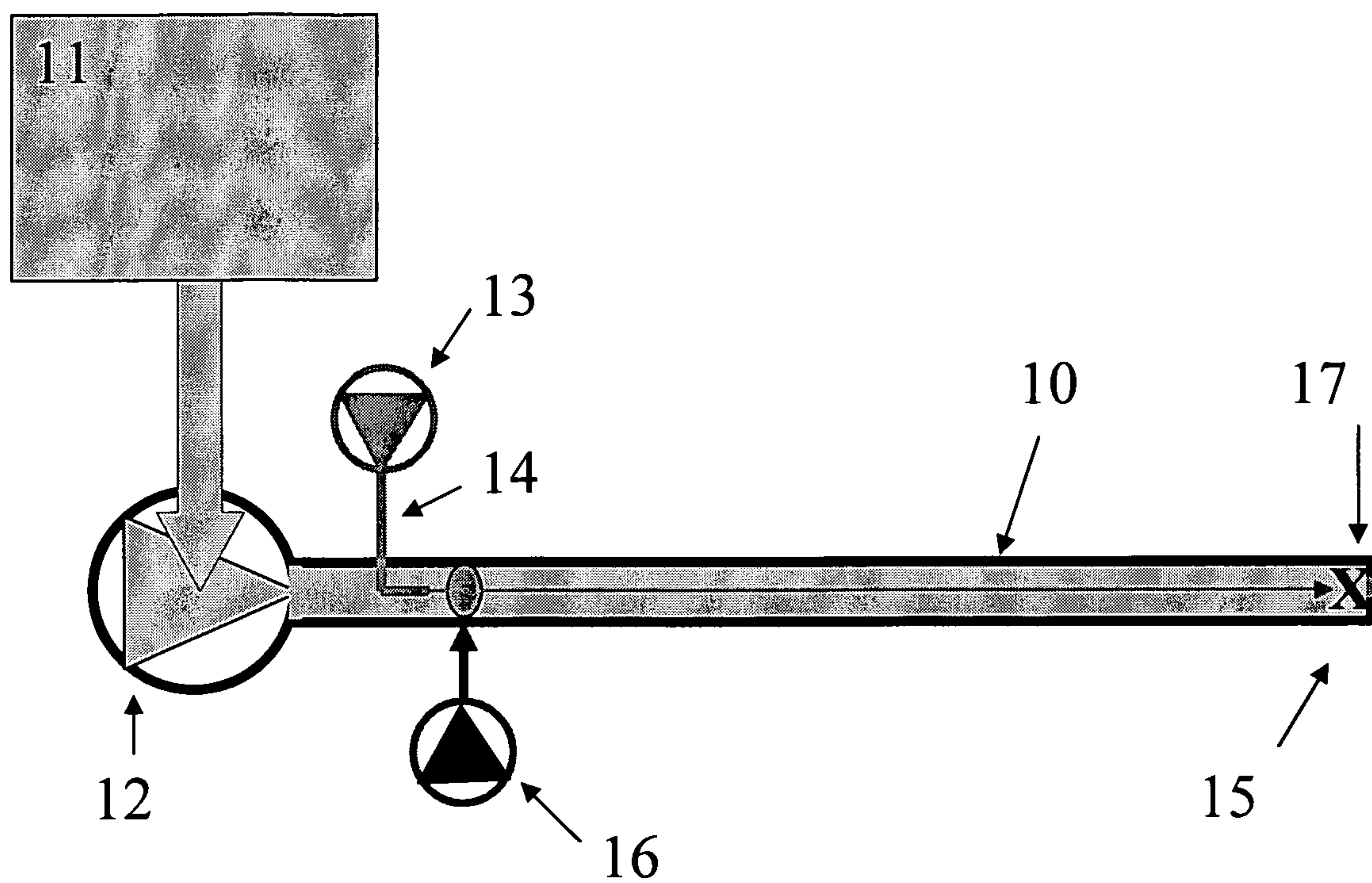


Figure 1

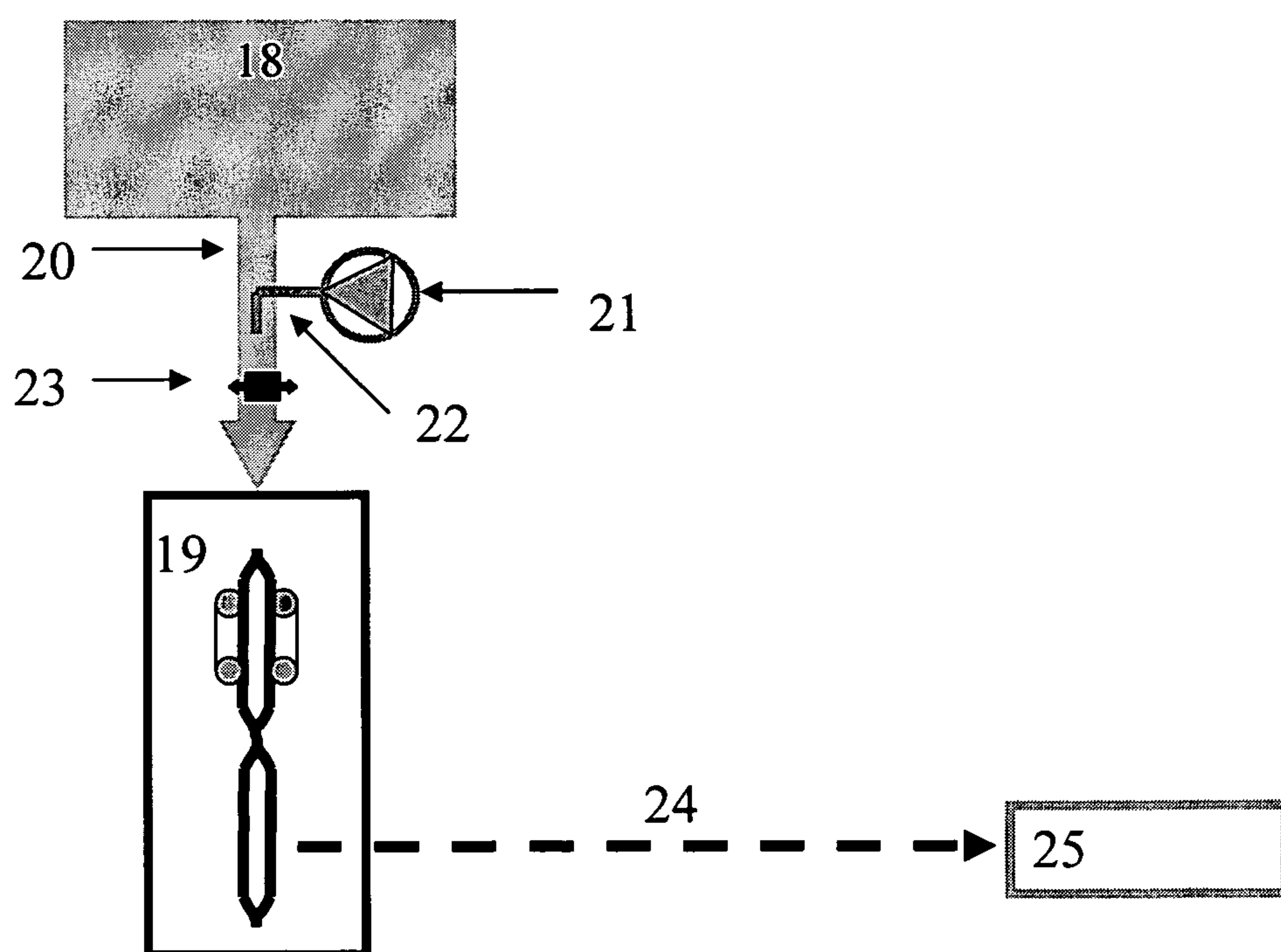
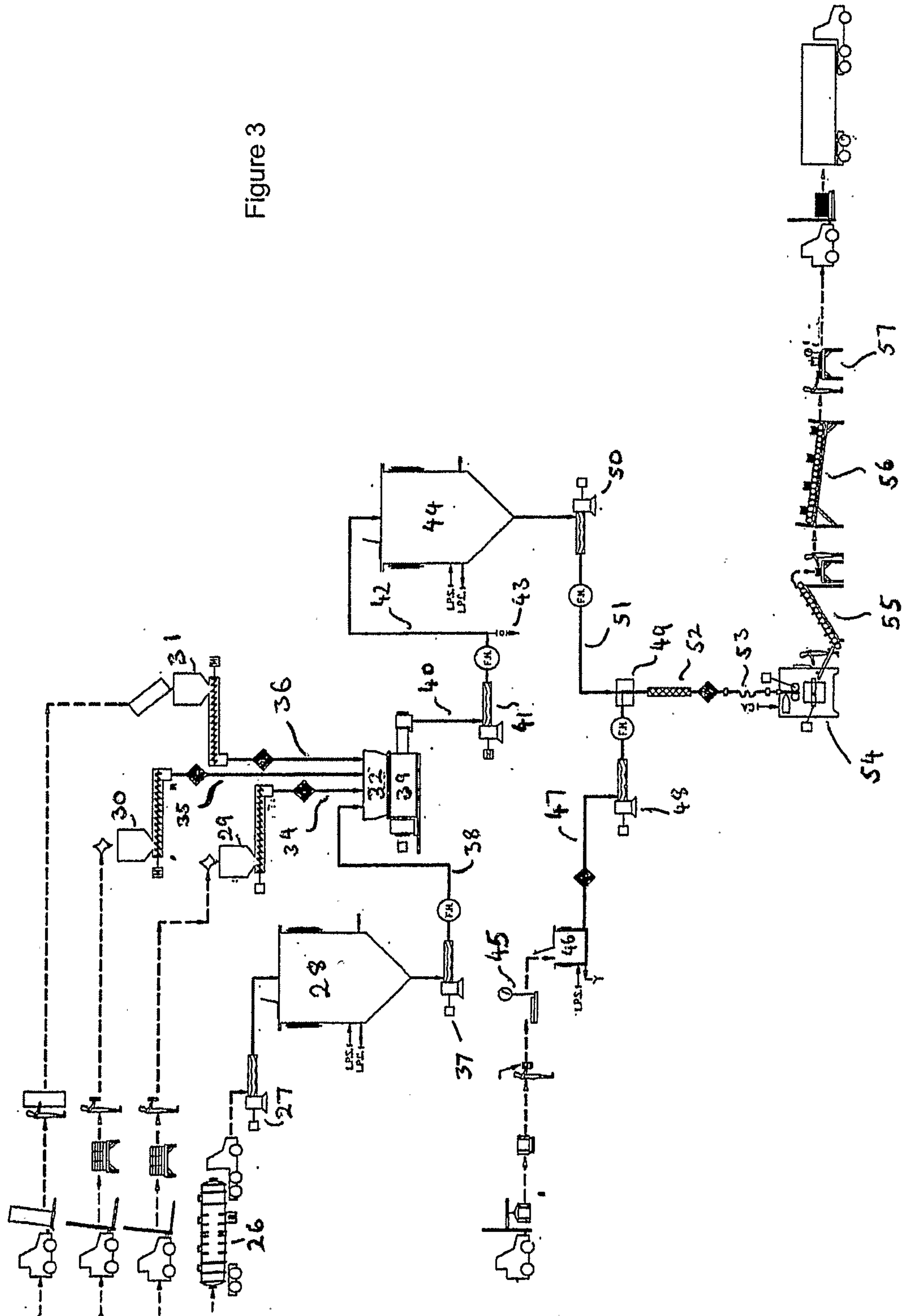


Figure 2

Figure 3



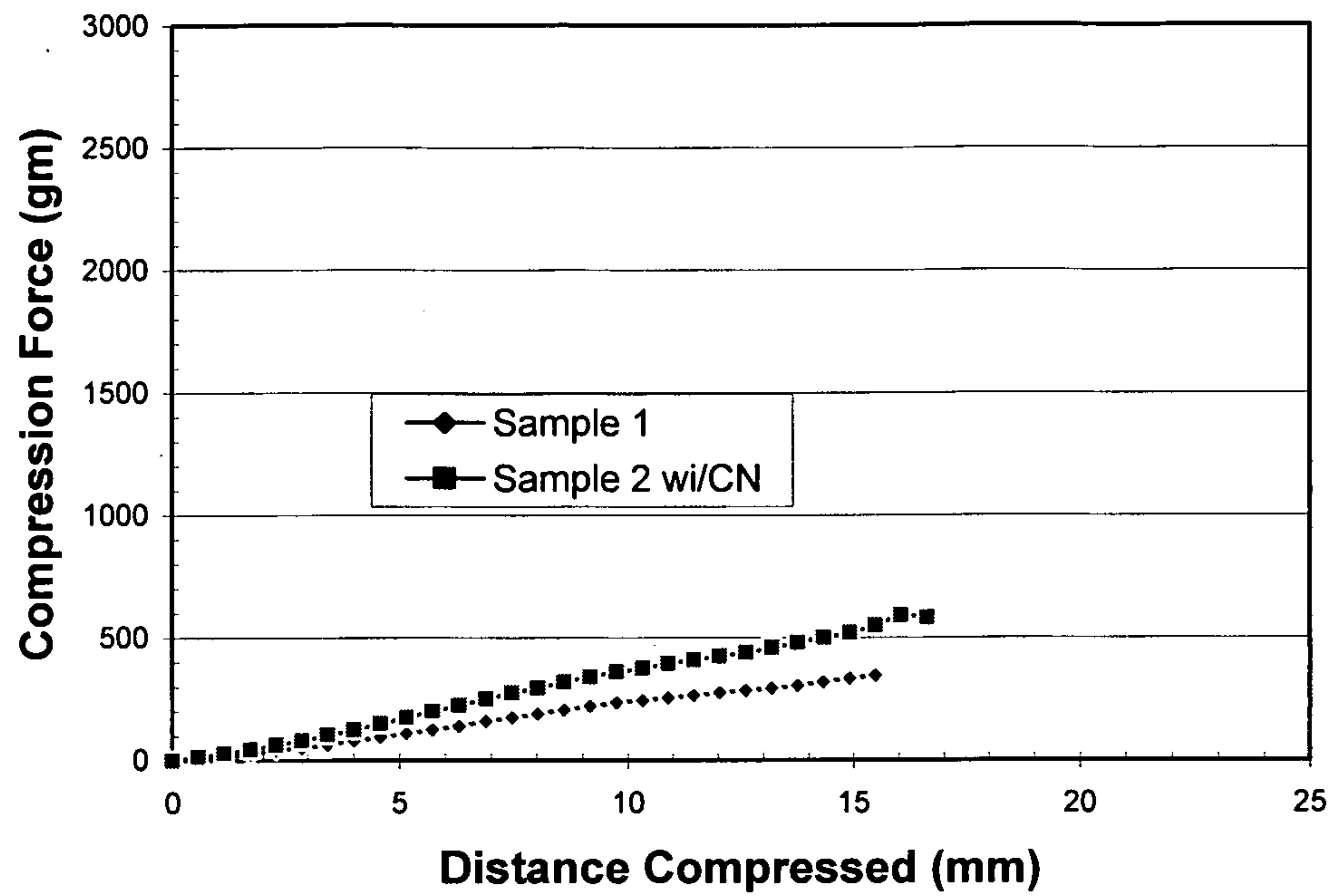


Figure 4

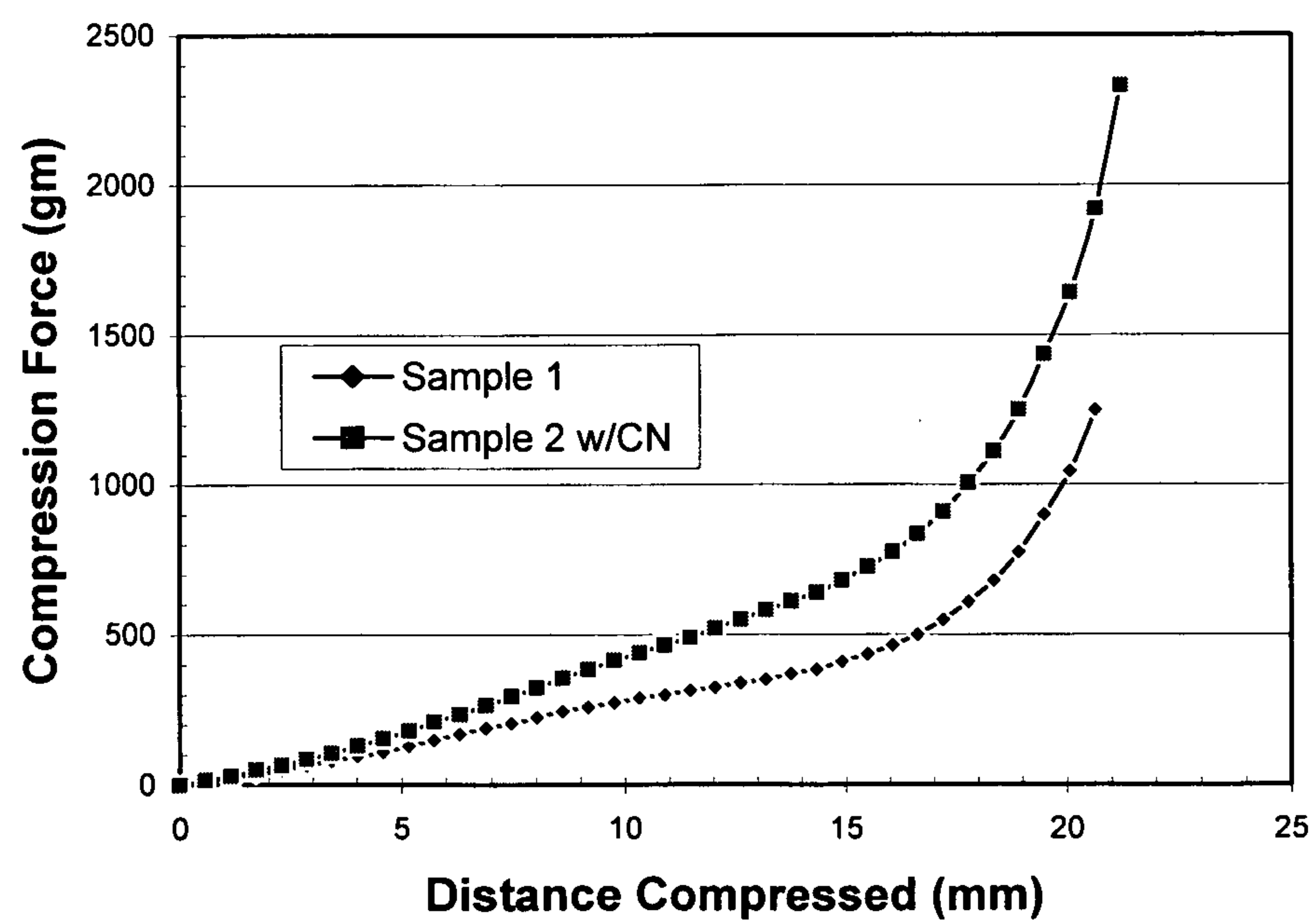


Figure 5

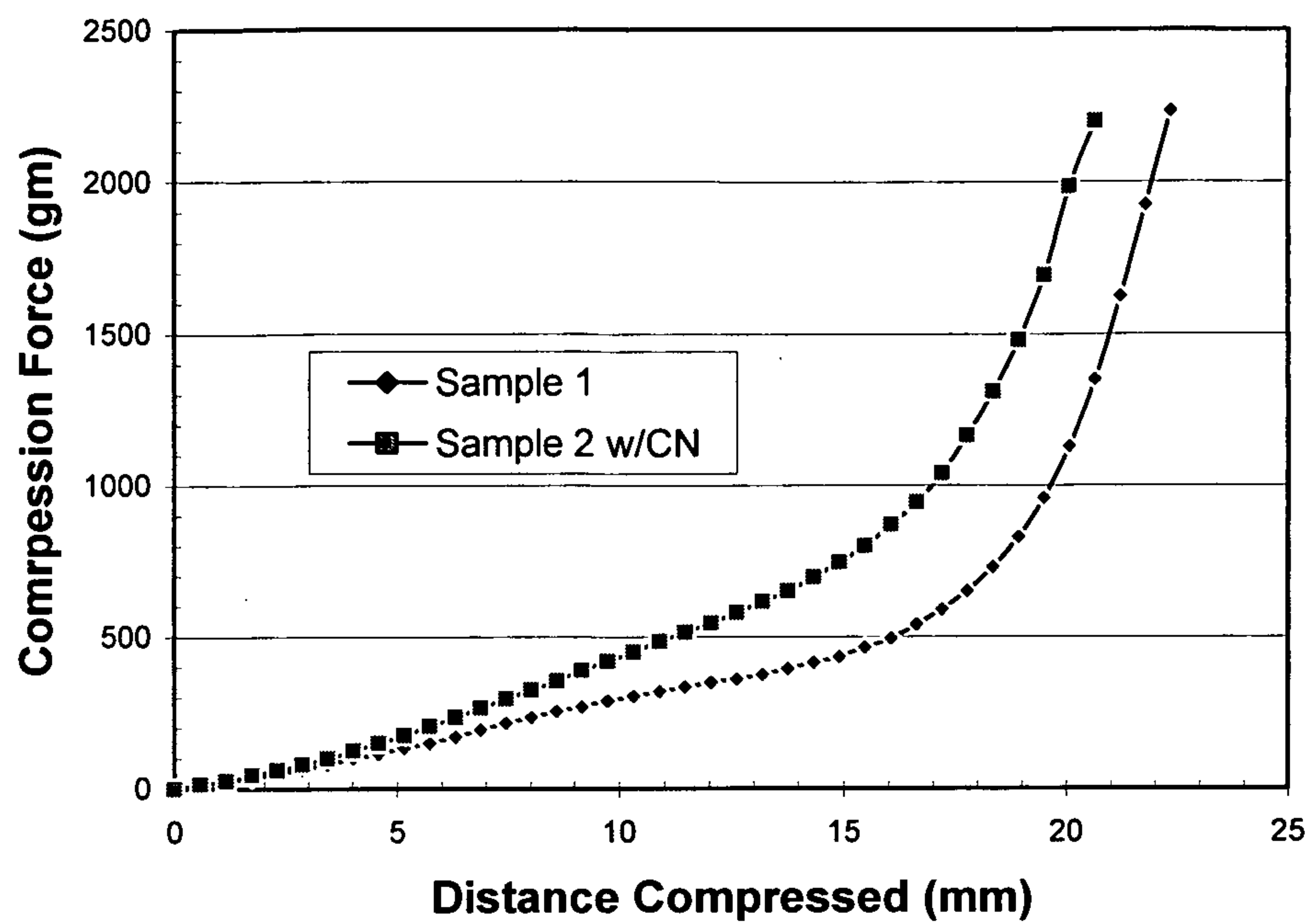


Figure 6

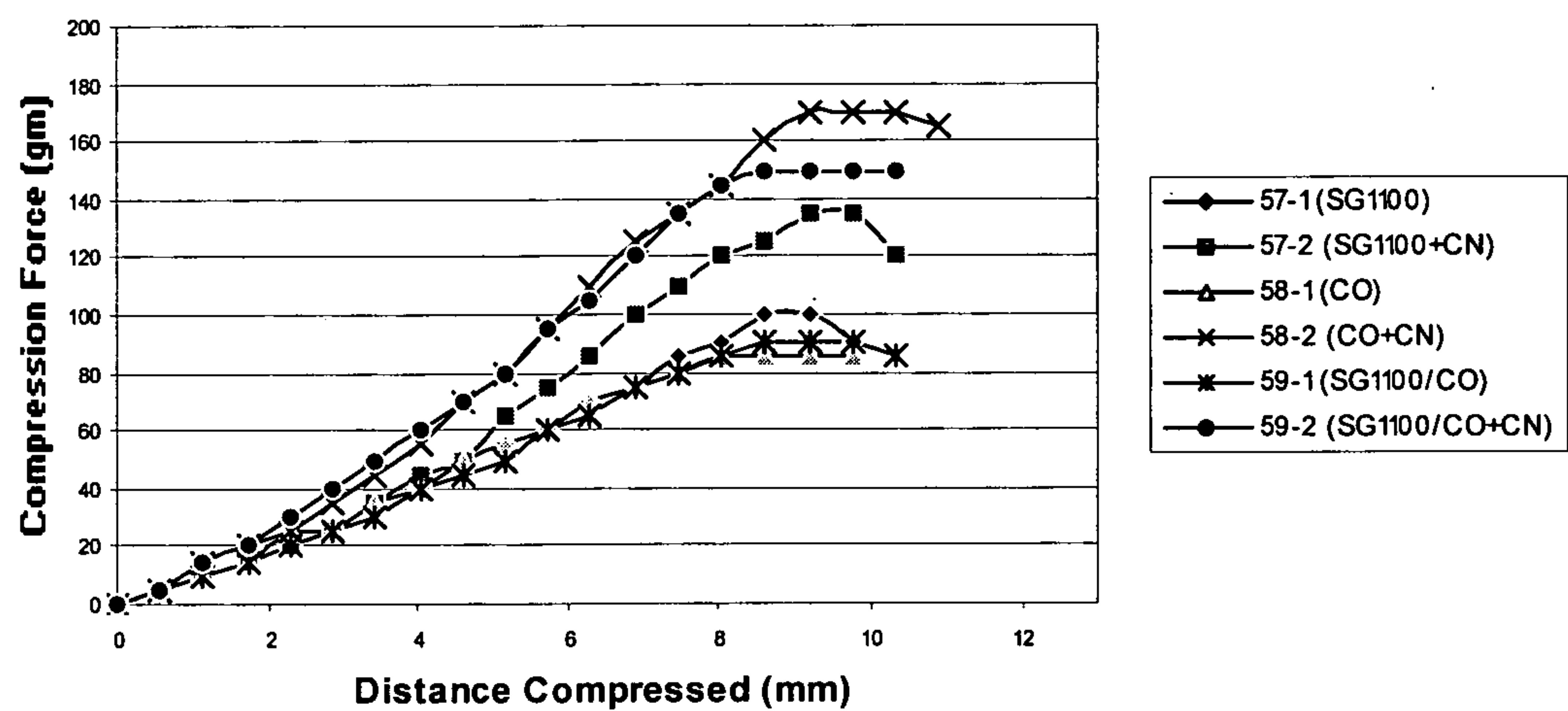


Figure 7

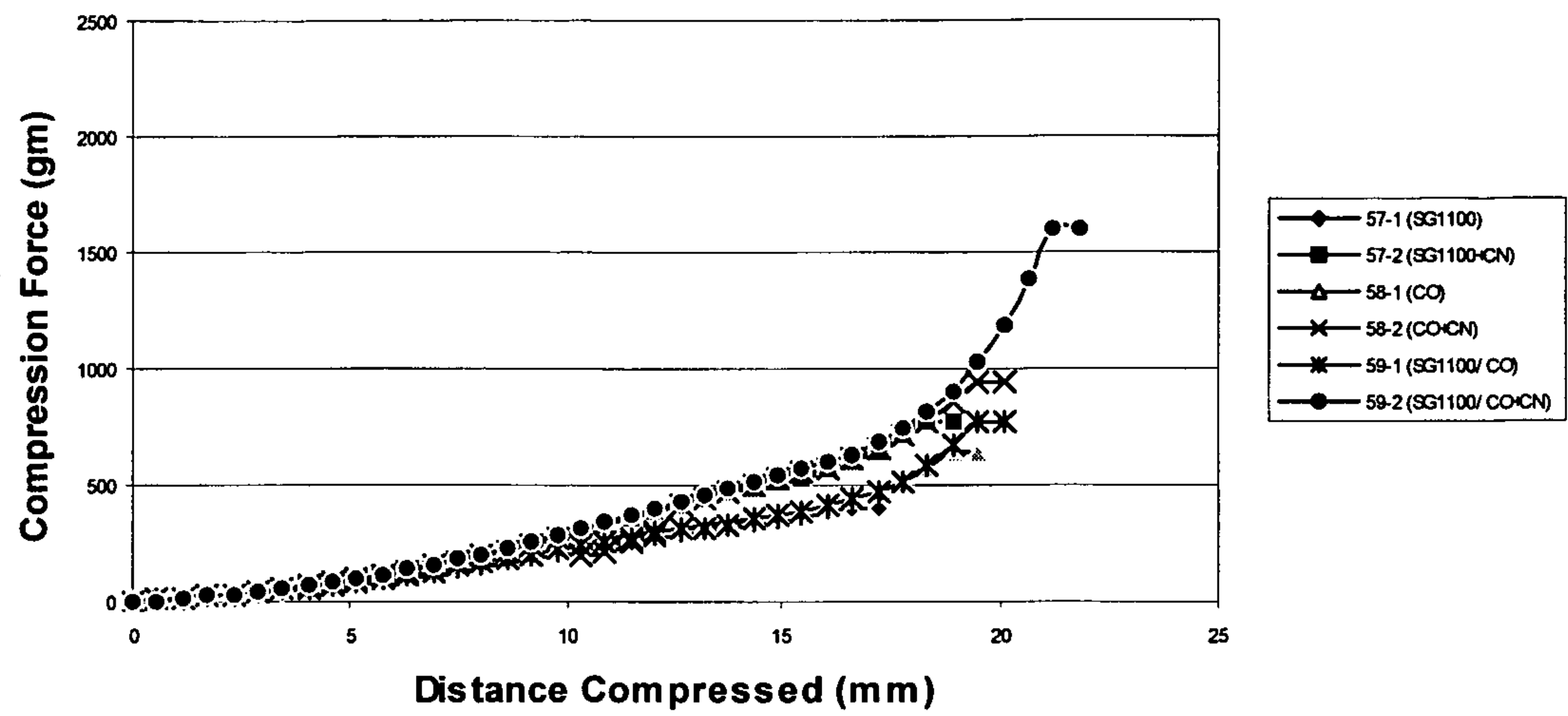


Figure 8

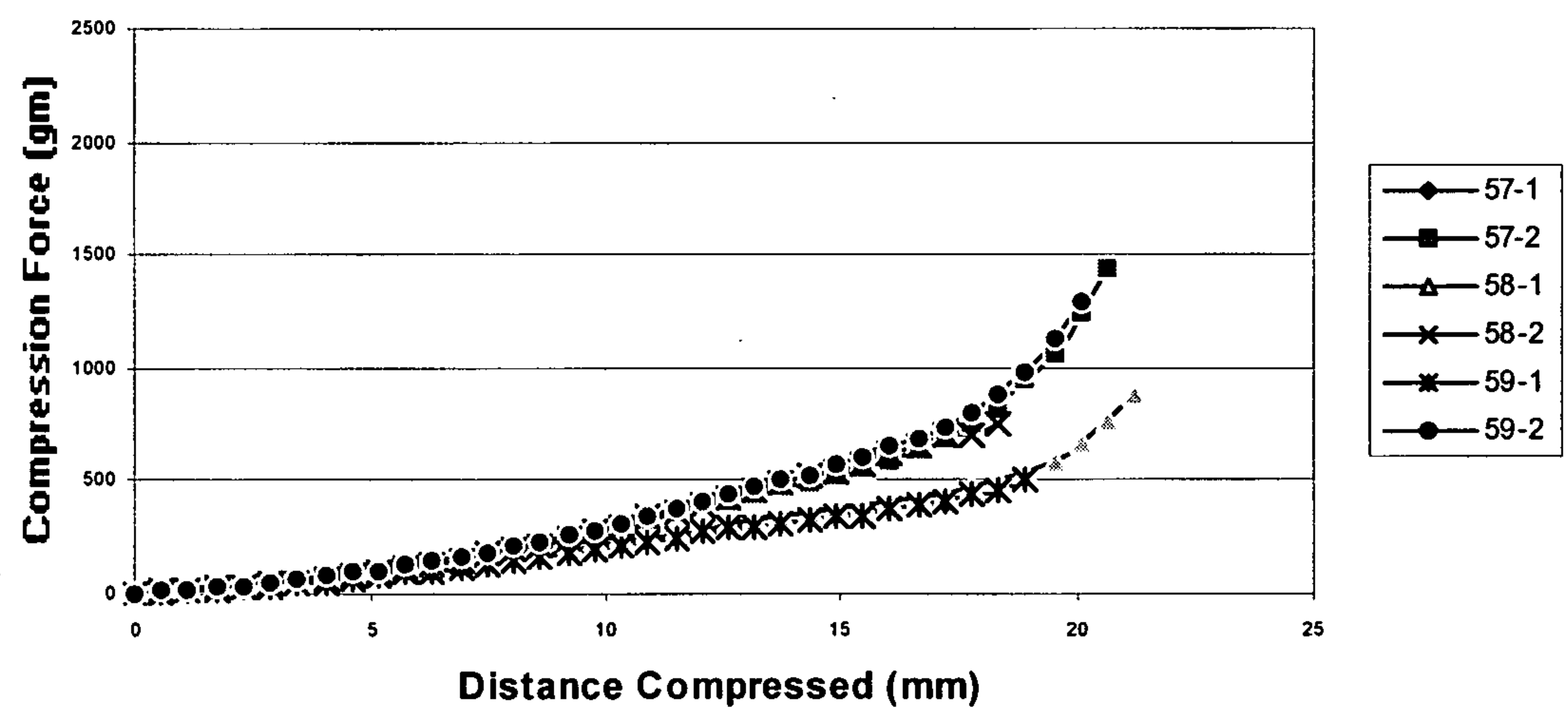


Figure 9