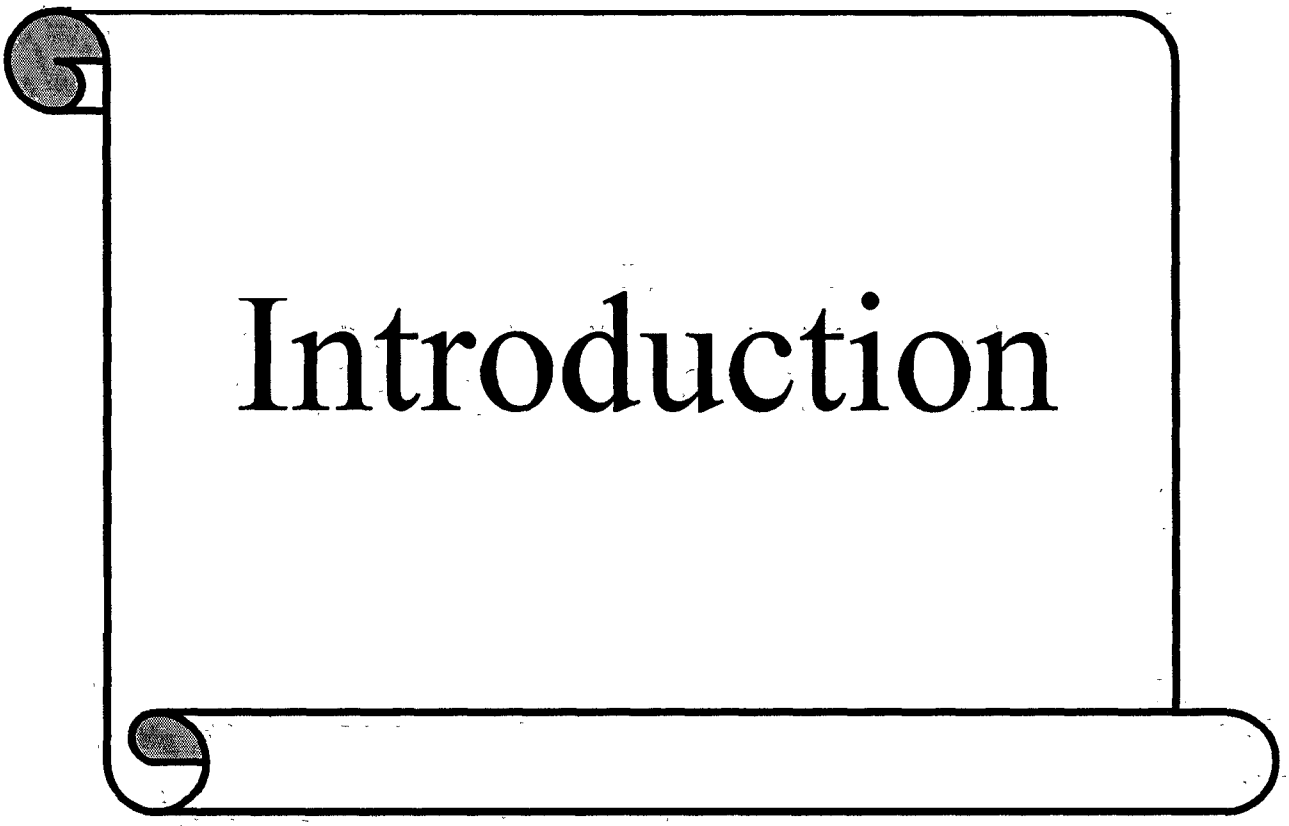
Introduction

I-INTRODUCTION

Until comparatively recently, individual greases were required for specific purpose but with the advent of new types of formulation, a wide range of application is now covered. This has resulted in the emergency of multipurpose industrial and automotive greases which are replacing the very numerous specified materials formally required.

We are hopeful that through this thesis, to make use of some products in the preparation of dielectric greases.

I-1-Greases Definition

Any oil mixed with either organic or inorganic fillers is called grease. Modern greases contain one or more fillers, base oil, additives and an optional tackifire, the later makes the grease sticky and increases adherence. The fillers hold the oil in its interstitial spaces, but it is the oil in the grease that actually lubricates [(1)].

Greases are products composed of a dispersion (liquid) medium which is retained in the cells of a structural frame formed by the solid particles of a disperse (thickening) phase with particles of colloidal size [(2)].

True grease consists of oil and/ or other fluid lubricant that is mixed with another thickener substance, a soap to form a solid. Greases are a type of shear – thinning or pseudo plastic fluid, that means that the viscosity of the fluid, is reduced under shear [(3)].

The three major components of grease (the base oil, a thickener and additives) are characterized. Important properties of base oil (its viscosity, cloud point and pour point) are examined. The three categories of grease thickeners (soap, complex soap and non soap thickeners) are described [(4)].

Lubricating grease consists of base oil, performance additives and a thickener which forms a matrix that retains the oil in a semisolid state. Most grease thickeners are soaps, i.e. (lithium, calcium, or aluminum soap). Complex soap greases have superior temperature resistance and are commonly usable up to 180°C, at which the mineral oil vaporizes. A smaller number of greases, restricted to very special applications, are manufactured with non-soap thickener such as organo clays, polymer or silica compounds. Grease is the most widely used lubricant for roller bearings and low viscosity applications mainly because grease type lubricants are relatively easy to handle and requires only the simplest sealing devices. The selection of the type of lubricant oil and the lubricating system depend mainly on: dropping point, maximum temperature, water resistance, oxidation stability, rust protection, pump ability and extreme pressure [5].

Lubricant grease is usually a mixture of 85 to 90 percent mineral oil or synthetic oil together with a thickener. In a majority of all greases the thickener is metallic soap. One example is lithium stearate for lithium soap. The function of the thickener of metallic soap is to hold the lubricating oil in a semi- liquid state for easier handling. When there is a rise in temperature, the oil bleeds out from the thickener and function as a lubricating agent. When the temperature drops again, the thickener soaks up the oil again to become semi–solid once more.

The type of greases chosen for a particular bearing lubrication application must therefor is chosen very carefully. High temperature greases used in low temperature applications may cause the bearing to seize due to lack of lubrication because the oil does bleed out. The common types of grease in use for rolling contact bearing are the calcium, sodium and lithium greases [6].

Lubricating greases are semi- solid lubricants they are consist of thickening agent which may be of an organic or inorganic nature in a liquid lubricant. Sometimes additive for special purpose are used. In order to obtain grease with required properties the correct choice must be made of the thickening agent and the fluid. More over the preparation of the grease should take place under carefully controlled condition so as to build up the correct "skeleton" in the liquid and to obtain the most stable grease. The "consistency" of the grease can be determined by measuring its "Penetration" i.e. the depth at which a metal cone penetrates into the grease under specified condition.

Sometimes lubrication with grease is to be preferred over lubrication with oil for the following reasons:-

A) A grease, if properly used, will not leak from the bearing, because it's a semi-solid material. This result in longer period of use and thus lower maintenance costs. Particularly in the case of bearing which are only accessible with difficulty, long periods between changing of the lubricant constitute an advantage.

B) Dripping and spattering are almost eliminated, even on shafts in vertical position, while the design of seals is simple.

C) Greases act as a seal against the entrance of dirt and dust which is especially important for such industries as for instance, cement, artificial fertilizer factories and textile industry.

In cases where lubricating oil acts as a coolant, greases can not be used because they don't sufficiently transfer heat [7].

I-2-Composition of greases

The essential components of grease are base oil and thickening agent. Grease may also contain additives and

fillers. The quality of the ingredients and the conditions of mixing determine the characteristics of the product.

I-2-1-Base oil

The liquid lubricating portion of grease generally represents 90 % of its total weight and constitutes an important factor in its performance

The characteristics of base oil (viscosity, volatility, etc....) will obviously influence the characteristics of the grease. Consequently the choice of the base oil (many may be used) should always be made in accordance with the intended use of the grease. Last of the time, we use mineral oils they offer good quality of low price. Synthetic oils are also used, above all when certain characteristics are sought such as for oils used in higher or lowers than normal temperature ranges. Vegetable oil are chosen for biodegradability, for contact with natural rubber is necessary or for lubricant which come in contact with food [8].

From manufacturing point of view, base oils can be classified as follows: mineral oils, synthetic oils and semi – synthetic oils.

I-2-1-1-Mineral oils

Mineral bases are manufactured from crude oil which has undergone a verity of complex separation operations. They are relatively inexpensive and deliver" average" Performance. They are so far the most commonly used, for both automotive and industrial applications.

Mineral oils will continue to be the fluids employed in the manufactures of the great bulk of lubricating greases; this is true because of the availability and low cost of these mineral oils [9].

Mineral oils consist of varying proportions of paraffinic, naphthenic and aromatic hydrocarbons. The trend in lubricating oil refinement is to produce oils which are more selective in composition to certain applications.

The manufacturing of the important transformer oils begins with the choice of the proper crude oil type i.e. naphthenic, paraffinic or mixed base. It has been conventional world wide and since many decades, to use naphthenic crude containing low concentration of paraffins, but all crude oil can be treated by certain processes to produce suitable transformer oils [10].

Transformer oil is usually refined mineral oil that is stable at high temperatures and has excellent electrical insulating properties. It is used in oil filled transformers, some types of high voltage capacitors, fluorescent lamp ballasts, and some types of high voltage switches and circuit breakers. Its functions are to insulate, suppress corona and arcing and to serve as a coolant [11].

Oil of the naphthinic group has traditionally been favored for using in insulating high voltage (HV) and extra - high voltage (EHV) cables, because of its good gas absorbing properties [12].

The lube oils can be subdivided into:

-Low viscosity index (LVI) oils.

-Medium viscosity index (MVI) oils, which according to their origin classified as MVIP (ex. Paraffinic stocks) and MVIN (ex. Naphthinic stocks).

-High viscosity index (HVI) oils.

The distillates in each group are graded according to their viscosity.

I-2-1-2-Synthetic oils

Synthetic bases, or synthetics, are products created by the chemical reaction of several ingredients. Two main families are used for lubricant formulation: Esters and synthetic hydrocarbon, in particular polyalpha olefins manufactured from ethylene. These products have excellent physical properties and exceptional thermal stability.

Synthetic oils, produced by complex chemical processes are more expensive. However, they deliver "premium performance" high viscosity index, better thermal strength and more oxidation resistance [13].

Seven main types of synthetic oils as:- Poly alpha-olefin (PAO), synthetic esters, poly alkylene glycols (PAG), Phosphate esters, alkylated naphthalenes (AN), Silicate esters and ionic fluids [14].

I-2-1-3-Semi- synthetic oils

Semi- synthetic oils are a mixture of the above two types of bases (generally 70 to 80 % inorganic oil and 20 to 30% synthetic oil).

I-2-2-Thickeners

The thickener has greatest influence on the character of the grease. This is why greases are classified by the type of thickener used. Thickeners form a fibrous structure which holds oil as a sponge holds water. There are two types of thickeners: metallic soaps and thickeners without soaps. Metallic soaps are used in 90 % of greases and may be subdivided into two categories: conventional soaps (lithium, calcium, aluminum, sodium) and complex soap. There are several sorts of thickeners without soap such as inorganic thickeners (clay, for example), polymers (poly urethane, for example), pigments, colorants, gels and waxes.

The soaps used to make grease are manufactured by saponification. Fatty matter reacts chemically with so – called alkaline metals during the production cycle. The fatty matter is generally consists of animal, vegetable or marine greases and oils. The most common alkaline metals (basic as opposed to acid products) are hydroxides of lithium, calcium, sodium and aluminum. Presently, the most commonly used saponifiable matter is 12- hydroxyl stearic acid, derived from castor oil, available in the form of acid or glyceride methyl ester: this is used above all for the production of lithium and calcium greases. Grease is not thick oil, but thickened oil [15-19].

I-2-3-Additives

Additives can play several roles in lubricating grease. These primarily include enhancing the existing desirable properties, suppressing the existing undesirable properties, and imparting new properties. Boundary lubricant such as molybdenum disulfide or graphite may be suspended in the grease to reduce friction and wear without adverse chemical reaction to the metal surface during heavy loading and slow speeds [20-22].

Although a limited number of greases contains only two components: the base oil and thickener, the better part of greases contains several additives to improve or modify their characteristics. As for oils, additives are used for antioxidant, anticorrosion and anti-wear purpose among others.

Additives technologies differ significantly from greases and oils, mainly the presence of thickeners in greases may interfere with the action of additives their concentration is often higher and hence the choice is much more limited. Solid additives form a film on metallic surfaces to reduce friction and prevent direct contact between surfaces [23].

Additives are added to lubricating greases to improve specific properties. Such compounds are corrosion and rust inhibitors, antioxidants, color stabilizers, viscosity index improvers and wear prevention [24-25]. Many chemical compounds are employed as antioxidants; sulphur and / or phosphorus – containing molecules are frequently used. Probably the most common types are aromatic compounds containing either a phenolic group (2, 6–di-tert-butyl–4-methylphenol) or amine group or both.

The fundamental point is that the inhibitor itself should be susceptible to oxidation and that oxidation products don't initiate oxidation of the hydrocarbons, it is eliminating, or at least slowing down lubricating oxidation. Increasing the time between oil changes though improved resistance to high temperature.

Antiwear additives reinforcing the antiwear action of a lubricant on the parts they lubricate. The mainly family of antiwear additives is alkyl zinc di-thio phosphates and numerous phosphorus derivatives. Corrosion – inhibitors, prevent corrosion of ferrous metals under the combined effects of water and atmospheric oxygen [26].

Qin, H. and Zhang, Q., prepared a grease consist of a lubricating base oil (98-99.4), ≥ 1of fatty acid epoxy resins, glycride oleate or butyl oleate (0.3-0.8), and an antioxidant such as 2,6-di-tert-butyl-4-methylphenol (0.2-1)Wt. %. The composition is superior in high durability and increasing surface brightness of rolled steel strips [27].

I-3-Classification of greases

In the manufacture of greases, mineral and synthetic oils are employed as the liquid base. According to the type of thickener, they are divided into: soap greases (conventional soaps and complex soaps) which are thickened by soaps (organic salts of sodium, calcium, barium, lithium and lead), hydrocarbons grease (gels, wax,

and paraffinic wax) thickened by paraffins, petrolatum and ceresin. Inorganic greases thickened by bentonite clays, graphite and molybdenum disulphide. Polymeric greases which are thickened by high molecular compounds, pigment and colorants greases.

The principle functional characteristics of greases are determined mainly by the thickener, through it is added in a relatively small amount (5 to 30 parts) while the dispersion medium is less decisive. For instance, a grease thickened by ceresin, whose melting point 75 °C, can operate at temperature up to (60-65 °C) irrespective of the type of oil used in it (petroleum oil or synthetic).

By applications, greases are divided into the following main classes: antifriction greases, friction greases, protective greases and dispersing greases. The major portion of greases relates to the antifriction class, many of the other possess high protective properties and are called all-purpose greases.

Some grades of greases possess unique properties, for instance, greases thickened by perfluorinated alkyl polyesters or poly tetrafluoro ethylene (Teflon) don't react with hydrocarbon, jet fuels, hydrazine, hydrogen peroxide, fuming nitric acid and liquid oxygen. The process of manufacturing of greases includes the following operations: preparation of components (fusing, dehydrogenation and preheating to the specified temperature), batching components in a reactor compounding, cooling and discharging (pouring). The quality of greases and the strength of the colloidal structure depend on the composition and what is most important on the condition of cooling [28-35].

I-3-1-Greases according to type of thickener

I-3-1-1-Metallic soap greases

Soap greases which are thickened by soaps (organic salts of sodium, calcium, barium, lithium and lead).

Metallic soap greases are usually prepared from (sodium, calcium, barium, aluminum, lithium and lead and barium) soaps and mineral oil. Mixture of these soaps is also used as complex soap greases. The fatty acids of these soaps are mostly saturated and unsaturated with a chain length is mainly between C_{14} and C_{20}. In certain cases hydroxyl fatty acids are also used.

I-3-1-1-1-Conventional soap greases

The metallic radical of the soap largely determines the characteristics of the grease, the fatty radical having a secondary effect. Greases are therefore classified in terms of the metal they contain.

An experimental greases has been formulated with 8.5 % (lithium 12– hydroxyl stearate in a base oil containing an additive composition of a synergistic blend of zinc dialkyl dithiophosphate, zinc diamyl dithiocarbonate, aromatic amine phosphate, sulfurized sperm oil substitute and the reaction product of coconut oil and diethanol amine. The lithium 12 – hydroxyl stearate grease has been prepared by a standard kettle procedure. The grease composition exhibits a dropping point in the range expected of lithium complex grease. The grease keeps its soap fiber structure intact at (390-400 °F) typical of the melting range of lithium 12–hydroxyl stearate greases. The grease is usually has long life in constant velocity joints [36].

A lubricating grease comprises a lubricating oil, from 5-30 percent by weight of an alkaline earth metal soaps of a mono or dihydroxy substantially saturated fatty acid containing from 12 to 24 carbon atoms, and up to 10 percent

by weight of an alkaline earth metal salt of an acid having a molecular weight below 160. Low molecular weight acids specified are acetic, propionic, boric acids and hydroxyl acid mentioned are hydroxyl stearic , such as the 9-10 dihydroxy and 12 mono hydroxy acids, and mono or dihydroxy lauric , myristic , palmatic and behenic acids .

The lubricating oil is preferably a mineral oil but synthetic oils such as esters of diboric acids and the polyglycol may be used. Plasticizing agents such as a non parafinic wax for example carnoba or candelilla wax, Corrosion inhibitors such as phenyl alpha naphthyl amine and other conventional ingredients may also be added to the composition [37].

A Comparative study on the preparation of some lithium greases from virgin and recycled oils based on soybean soaps stock as an alternative of tallow. The utilization of recycled oil in the preparation of lubricating greases improves their physical and mechanical properties[38].

I-3-1-1-2-Complex soap greases

In general, a complex soap greases thickener is made by reacting an acid, alkali and dibasic acid to give the complex soap. For example, 12–hydroxyl stearic acid, lithium hydroxide and azelaic acid to give lithium complex.

Witte J., et al. have pointed that lithium complex grease composition which contains a certain weight ratio of calcium acetate are provide which demonstrates a constant viscosity over a wide temperature range . Comprised of a major amount of lubricating oil and form about 15 to 35 weight percent based on the grease composition of a mixture of calcium acetate and lithium complex soaps (lithium 12-hydroxy stearate and lithium azelate) in 1.2:1 to 1.7:1 weight ratio respectively [39].

Ullmann, D. and Grasshoff prepared a calcium soap lubricating grease comprising lubricating oil and calcium

soaps, the calcium soap being prepared from fatty acid, calcium hydroxide, sodium phosphate and sodium borates[40].

Coleman, et al. made a patent of grease useful at high temperature (high dropping point) composed of aluminum complex soap thickened greases having selected consistency, water resistance, and anti- wear properties [41].

Synthetic fatty acids may be used in the preparation of high quality complex calcium grease hence; it will be capable of operating over a wide range of temperature. Synthetic complex greases based on the soaps of C_{10}-C_{20} and C_{17}-C_{20} production have fairly high tensile strengths at 50-80 °C, low viscosity at 0 °C and good water stability. Complex calcium grease may be used as universal purpose greases suitable for use in various mechanics operating under different operational conditions [42].

Lubricating grease composition based on titanium complex soap thickener in mineral and synthetic oils has been prepared for the first time. Tentative methods for preparing lubricating grease from this new type of titanium complex soap thickener have been described. High performance lubricating grease resulted from titanium terphthalate stearate complex soap thickener [43].

Stuart J. and Janes A., prepared a lubricant grease composition including the combination of an oil base, a thickener and bismuth preferably in the form of bismuth carboxylate. The grease has excellent fil‹ strength improved (anti - washout) capabilities and depending on the thickener used, may have no dropping, meaning that the oil will not separate out at elevated temperatures [43].

I-3-1-2-Non- soap greases

Instead of soaps, inorganic compounds (silica, clay, pigments) or organic compounds (waxes and / or polymers) are sometimes used to thicken a liquid lubricant. In some cases this non-soap – base grease may show an advantage over soap – base greases.

Nonsoap thickeners are also gaining popularity in special application such as high – temperature environment. Bentonite and silica are two examples of thickeners that do not melt at high temperature. There is a misconception, however, that even though the thickener may be able to withstand the high temperatures, the base oil will oxidize quickly at elevated temperatures, thus requiring a frequent relube interval [20-22].

I-3-1-2-1-Hydrocarbon greases

Hydrocarbon greases are thickened by paraffin, petrolatum and ceresin. Paraffin wax, microcrystalline wax and petroleum ceresin are petroleum products which are should at room temperature and which consist of certain range of n – paraffin wax (also called crystalline wax) is predominantly macrocrystalline. It is composed mainly of n-paraffins of the melting point range (33- 71°C) and small amounts of iso- (and / or cyclo) paraffins and oil.

Microcrystalline wax (also called plastic wax) has a microcrystalline structure. These types of wax consist mainly of high molecular weight iso – (cyclo) paraffins. Their melting point ranges from (71 to 93°C). Microcrystalline wax with high oil content is called petrolatum or petroleum jelly.

Petroleum ceresin, ceresin have a very dense microcrystalline texture. They are composed mainly of high molecular weight n- paraffins and branched hydrocarbons (m.p. range lies between 82-104 °C), they are very hard and brittle [43, 44, 45].

An electric insulating composition, suitable for impregnation of an electric cable dielectric designed to work at temperature up to 80°C, was prepared by incorporating a proportion of polymerized ethylene in petroleum jelly or in mixture of petroleum oil with paraffin wax [46].

David M. M., prepared a synthetic petroleum by mixing a distillate lube oil, slack wax and a wax crystal modifier having an intrinsic viscosity of (0.1 – 0.3 dl/g). Suitable modifier includes amorphous poly propylene, amorphous poly ethylene and ethylene–isobutyl acrylate polymer [47].

A cable greases has the following composition in percent by weight: mineral oil(9-10), ozocerite(27-30), pentaerythritol ester of C_6-C_9 , synthetic fatty acid (25-80), sulfurized nigrol (23-70) , oxidized petrolatum (9-11) , poly isobutylene (0.3-0.5) and diphenyl- amine(0.3-0.5) [48] .

In an American patent, a lubricating greases is prepared by the reaction product of significant amount of fish oil , a sulfur modified sperm oil , a microcrystalline wax and an oxide of lead , the lubricating greases additionally comprise up to 90 % by weight of a hydrocarbon oil which result in an extreme pressure grease lubricant having a desirable lubricating properties [49].

In another American patent a synthetic and natural lubricating oils were mixed with microcrystalline wax having melting point about (50-75°C) and blended with about 70 to 50 parts by weight of an aliphatic ester component derived from the esterification of aliphatic alcohols , diols and polyols or their ethers by aliphatic mono or dicarboxylic acids. The composition can contain from about 0.5 to 5 parts by weight of one or more extreme pressure or load bearing additives [50].

Kim, J., made a patent on grease useful at high temperature composed of a wax isomerate based base stock

plus an antioxidant consisting of a metal salt and a diphenyl amine. The base stock may be 100 % wax isomerate oil or a mixture of wax isomerate oil and mineral oil [51].

Two wax samples which are macrocrystalline wax (paraffinic wax) and microcrystalline wax and two oil samples which are medicinal white oil and imported medicinal white oil were used to produce petroleum jelly with medicinal grade [52].

Kinicad, prepared grease which was used in telephone cable by mixing a low–d-cellular polyethylene, filled with petroleum gel and sheathed black medium d-polyethylene[53].

A cable lubricant was composed of (wt %), 20 atactic polypropylene , 10 transformer oil , 10 cylinder oil , polyethylene , 80 petrolatum ceresin wax, 57 petrolatum [54].

A grease containing paraffin wax, Japan wax, polyethylene wax, polyethylene acrylate wax or a mixture of any two or more of these and water resistance materials with poly(vinyl alcohol) and optionally a polyamine is obtained [55, 56].

I-3-1-2-2-Polymeric greases

They are thickened by high – molecular compounds.

Brauer, et al. prepared a grease compatible extended polyurethanes comprising the reaction product of polymethylene polyphenyl isocyanate with a polyol is hydroxyl terminated polybutadiene in presence of a cyclic olefin extender (poly cyclic pentadiene) and a plasticizer (tridecycl adipate, diundecycl phthalate), soybean oil, glycryl tri(acetyl ricinoleate) or dibutyl phthalate. Certain extended polyurethanes are characterized as being reenterable, such that they can be used for encapsulation of electrical or telephone cables. Polyurethane greases were found to be soft, clear gels which are suitable for use in

applications such as encapsulation of electrical or telecommunication cable [57].

Meijer, D., et al, patented polymer thickened lubricating grease composed of a high molecular weight (co– or homo-) polymer of propylene. The patent further related to a lubricating grease composition comprising lubricating oil and the above polymeric thickener. Also, the invention relates to the use of such a polymer thickener in the preparation of lubricating grease compositions with improved oil bleeding characteristics at low temperature and improved noise characteristics and / or improved mechanical stability [58]

Tamakas, K. and Mansumori, Y., made lubricating grease from polyisoprene rubber (100) parts by weight, about (15-45) parts by weight of aliphatic amides or a specific group of aliphatic bisamides and (5-30) parts by weight of polyethylene wax, paraffinic wax and microcrystalline wax. A bull joint is disclosed that contains this lubricant composition [59].

Gerado, C. and Silverio, S., have developed a lubricant greases containing a mixture from 15% to 40% by weight of polytetrafluro ethylene, from 60% to 85 % by weight of liquid dispersing medium of the type of perfluro polyether or oligomer of C_2ClF_3 less than 1 % by weight of perfluro alkyl or polyoxy perfluroalkyl surfactant and optionally, stabilizing and anticorrosion agents of the class of polyoxy perfluro derivatives [60].

Fuks, I.G. and Bakaleinikov, M.B., showed that polyisobutylene favors the structurization of lithium, silica gel, and hydrocarbon greases regardless of the composition of the dispersion medium. The concentration of polymer in silica gel grease prepared with PN–6 oil must be at least 2 %, and in the hydrocarbon grease prepared with S-220 oil at least 3%. In the greases prepared with S-220 oil, the

addition of polymer (within the concentration range investigated) lead to softening of the greases [61].

Lin, Z. and Wangxinmin prepared a greases composed of a type of a tactic polypropylene is 3 % - 18 %, petroleum wax (10 %- 40 %), petroleum tar is (5 % - 30 %), Lenolinc metal soaps anti-rust (1% - 7.5 %) and mineral oil is allowed. Because heavy polymer a type of a tactic polypropylene which can be dissolved in the oil used, the dripping spot of alkyl consistent grease rise above 80 degree[62].

Hassan, A.M., et al. studied the electrical properties of different sample of poly(vinyl chloride) grease which were formulated from poly(vinyl chloride), Refox 65 as plasticizer, and a wax gel (transformer oil and wax) with variable proportions of phenyl formaldehyde, stearyl phenol formaldehyde or stearyl phenol formaldehyde urethane resins [63].

A lubricating grease comprised of 2 to 8 % by weight of an aluminum fatty acid soap, 125 to 98 % by weight of a polymer of a non hydrogenated polyisobutylene having a mean molecular weight ranging from 300 to 2500, 0.2 % polyisobutylene having a mean molecular weight higher than 100.000 and a bout 58 % of lubricating oil [64].

A vinyldiene fluoride–hexafluro isobutylene copolymer powder is employed to thickener conventional fluorine containing a liquid lubricant to provide a grease composition which has improved lubricating character in metal bearing subjected to the simultaneous conditions of high load, high speed and elevated temperature [65]. Silicon grease is made by combining silicone oil, with a thickener. Most commonly, the silicone oil is polydimethyle siloxane and the thickener is amorphous silica.

A grease composition containing a polysiloxane, the organic substitutes of which are primarily methyl radicals

and C_6 to C_{20} alkyl radicals, a thickener and zinc naphthalate. The presence of the zinc naphthalate in the grease provides a corrosion resistance to iron and alloy metal surfaces to which the grease is applied [66].

Vinci, J.N., et al. prepared a grease consist of a lubricating base oil and a total of from ~1 to ~50 %by Wt. of copolymers. The copolymers consist of: (A) at least one ethylene-aliphatic olefins copolymer where the aliphatic olefin contain from 3 to ~24 carbon atoms, the copolymer (A) having M_n ranging from ~600 to ~5000, and (B) at least one copolymer comprising units derived from alkyl acrylate ester monomers containing from ~0.1% to ~20% by Wt. of at least one member of the group consisting of vinyl aromatic monomers and nitrogen containing vinyl monomers, the copolymer (B) having M_n ranging from ~10.000 to ~ 350.000[67].

I-3-1-2-3-Inorganic greases

Inorganic greases are thickened by bentonits clay, graphite and molybdenum disulfide.

Uematsu, T. and Ito, had recognized the highly thermal conductive grease composition. The grease composition comprises from 70-90 % by volume of inorganic powder (zinc oxide, magnesium oxide and boron nitride) and from 10 to 30 % by volume of boron containing a mineral oil or synthetic oil (α- olefin oligomers, diesters, polyol esters, alkyl phenyl ethers). The base oil further containing a surfactant in an amount of from 0.2 to 2.0 % by weight based on the weight of the inorganic powder [68].

George, G.C. and Westfield, N.S., prepared a lubricating grease having extreme pressure properties comprising a major amount of lubricating oil and minor amount of colloidal asbestos, finely divided polymeric fluro carbon powder and powdered inorganic grease thickener . The inorganic thickeners are selected from the group

consisting of talc, graphite and groups I, Π and IV of metal oxides and carbonates [69].

A grease composition for use as cable filling materials which contain about 75 to 95 parts by weight of a base component of a polyol or ester having a molecular weight of at least a bout 3000 and about 2 to 20 parts by weight of colloidal particle such as silica, clay or mixture thereof. Optionally about 1 to 3 parts by weight of an antioxidant component as irganox 245 can be added to impart high temperature resistance or rubber component as poly butadiene can be added to improve bleed resistance. Also, an article of manufactured of cable having a method for filling the cable with such grease compositions [70].

I-3-1-2-4-Pigment /colorant greases

Lubricating compositions containing color temperature indicators are disclosed. The compositions irreversibly change their color when exposed to temperature exceeding a predetermined limit temperature. The composition mainly includes from 0.2 % to 4% weight of metal dithio carponates or dialkyl dithio carbonates preferably of antimony and / or lead in combination with a dye, preferably a blue dye, in an amount of from 50 ppm to 2000 ppm. Other components, such as epoxy resins, may be also present to increase and / or extend the range of temperature of which the charges or color are observed. The composition useful as indicators of over heating of lubricated elements under sever operating conditions [71].

I-3-2-Greases according to the applications

I-3-2-1-Antifriction greases

Antifriction greases which lower friction and wear in friction pairs. In the Russian patent an antifriction greases based on organo silicon fluids and metal powder was distinguished by the fact that in order to improve the

effectiveness of the grease. Silver or gold powder was introduced into its composition as the metal powder. The powdered silver or gold is introduced in a quantity of 5-60 weight percent [72].

Shapovalvo, V.M., et al. presents the composition and the process of production of the new grease containing exclusively environmentally safe biodegradable components such as vegetable oil, fat as well as natural and artificial silicates. The grease is operable within (0-160°C) and intended for friction units of light and food industry equipments [73].

I-3-2-2-Friction greases

Friction greases which increase friction and prevent slippage (they are essential for the lubrication of belt transmission and the other similar uses).

A silicon elastomer compatible with constant velocity joint grease comprise a urea grease composed of lubricating oil and a urea thickener and an effective amount of a friction reducing an additive package comprising molybdenum oxy sulfide dithiocarbonate, polyphenylene sulfide and potassium triborate . The additive solids have particle size below about 40 micros [74].

I-3-2-3-Protective greases

They prevent corrosion. The method of producing protective grease by means of thickening its base is distinguished by the fact that an epoxy compound containing epoxy resin and polyethylene poly amine was used as thickening agent for the purpose of increasing the effectiveness of the grease. The base of grease is thickened by (29-31%) epoxy compound containing (100) pbw of epoxy resin and (10–12) pbw of polyethylene polyamine[75].

Fujiwara, et al. prepared a grease consist of ≥40 wt.% methylphenyl silicon oil and/or polyphenyl ether oil as

base oil for filling and/or coating in and/or on wires of cables for power line with corrosion protection [76].

I-3-2-4-Dispersing greases

They improve the alignment of mating parts.

Martin, A.J.E. and Valenica, C., study the feasibility of recycling polyolefins. They are used as additives to improve the rheological properties of lithium 12-hydroxyl stearate lubricating greases. The effects that both soap and recycled low density polyethylene (LDPE) concentration exertion the rheological lithium lubricating greases and its relationship with grease microstructure [77].

I-3-2-5-Unique greases

Dielectric greases are non- conductive grease. Because it is non conductive it does not enhance the flow electrical current. Dielectric grease is often applied to electrical connectors.

Dielectric greases and insulating fluids are insulating oils, greases, transformer oils and fluids that have a high dielectric strength are used in transformers, capacitors and other electrical devise applications. Adding dielectric grease to switch contacts and potentiometer tracks improves performance and operating life. Using synthetic dielectric greases on the pins, blades and sockets of separable electrical connectors goes a long way toward preventing wear, sealing out the environment, improving performance and extending the operating life of your electrical device [78].

Many years experience in Britain has shown that petroleum jelly, used as an insulator coating, is an effective against flash over in polluted localities. The broad classes of satisfactory material are petroleum jellies silicon greases are strippable compounds. Petroleum jellies were originally made from a wide range of petroleum fractions, but they are now generally compounded from hydrocarbon oils and

microcrystalline waxes. Materials with similar characteristics, containing some synthetic waxes, have also been included in this category. They often characterized by the increase of temperature and melting at sites of discharges. Silicon greases are composed of silica filler and silicon oil, which is the active component. They don't melt but they decompose at temperature above 200°C.

Strippable compounds are blends of waxes, oils and copolymers of ethylene-vinyl-acetate or ethylene-vinyl acrylate type [79, 80].

Fowzy and Mahmoud A., have developed perfluoro polyether grease containing different types of non-soap thickeners with PFPE base oil. This paper highlights the unique properties of PFPE (non reactive, nonflammable, safe in chemical and oxygen service and long lasting) as well as its unique application in areas where other lubricants are deficient [81].

Premium plus multipurpose marine grease for high resistance against winter, rust and corrosion is specially formulated as all- purpose grease for boats, boat trailers and other marine applications [82].

In American patent, silicon grease for semiconductors which useful to surround semiconductor junction as a heat transfer media was prepared by mixing 15 to 97.9 percents of a polysiloxane fluids, 0.1 percent of neutral, dielectric, strong desiccant being at least one selected from the class consisting of anhydrous calcium sulfate and synthetic zeolites from 2 percent to 84.9 grease thickening agent finely divided, non conducting inert oxides of metallic and glass metallic materials and inert organic thickening agent materials and mixture thereof substantially free of interfering water [83].

Fam, S.A., et al. prepared some new insulator greases from synthesized wax, blend of lube oil, resin or polymers,

antioxidant and anticorrosion additives in different ratios at various temperature and the produced greases were screened as insulators. At the highest ambient or discharge temperature likely to be experienced, some of the prepared grease were found to be efficient as insulator indicators [84-85]

Funahashi, et al. obtained a grease composition containing mineral oil and / or synthetic oil as base oil, (A) lithium stearate as thickener and, (B) one kind or two kinds of more of compounds selected from a group of oxidized paraffins and diphenyl hydrogen phosphate. The grease composed of low dust emission which performs with an excellent balance of low dust emission, and is suitable for use in a clean environment such as semiconductors manufacturing equipments, and electronic computers [86].

Hyde, B. and Cross Juncation, V.A., produced a petrolatum–based lubricant composition that is nonflammable and which includes an extreme pressure additive. The lubricant composition is suitable for marine and automotive applications. The composition comprises in percent by weight: 4 % carbon dioxide, (0.125 %) amine. (78 % - 81 %) trichloro ethylene, (10 % - 20 %) petrolatum, 0.44% methyl salicylate and (0.5 %) mono lube [87].

Niemi and Randolph G., prepared silicon composition by mixing polydimethyl siloxan fluid containing hydroxyl radicals , finally divided aluminum hydroxide filler , silane and an optional condition catalyst. The coating cures an exposure to atmospheric moisture to produce a surface adherence onto the insulator (high voltage) that resists the development of leakage currents and flash over failure upon exposure to electrical stress, moisture, contamination and other outdoor weathering stresses [88].

A lithium grease containing paraffin oils, thickeners and lithium compounds, which comprises crystallization modifier consisting of lattice modifiers formed by mineral

acids in percentage by weight between 0.01 and 5 % and polarity modifier of oil formed by alkyl (C_7-C_{20}) benzene, in percentage by weight between 0.01and 10 %, one aromatic extracts which are residues of extraction with furfural of lubricating oils in percentages by weight between 0.01 and 8% [89].

Kinoshita , et al. made a grease composed of a base oil selected from the group consisting of mineral lubricating base oils , synthetic lubricating base oil and mixture there of : (A) 2 to 25 % Wt. % , based on the total weight of the composition of a thickener selecting from a group consisting of urea compounds , urea-urethane compounds , urethane compounds and a mixture thereof and (B) 0.2 to 5 wt. % based on the total weight of the composition of an ingredient selected from the group consisting of oxidized paraffins, diphenyl hydrogen phosphate, hexamethyl phosphoric triamide and mixtures thereof [90].

The grease filled telephone cables were developed in order to minimize the risk of water penetration, which can severely upset electrical signal transmission quality.

Brown, Geoffrey David and Keogh , produce a grease composed of as a first component , a Plurality of electrical conductors, each surrounded by one or more layers of a composition comprising (a) one or more polyolefine are bonded there to or blended with , (b) a linear or cyclic organo polysiloxane containing one or more functionalized hindered amine moieties and as a second component , hydrocarbon cable filler grease within the interstices between side surrounded conductors [91].

Gartside , et al. prepared a grease consisting of (77 to 95%) by weight of paraffinic or naphthenic oil or polybutene oil, colloidal particle filler (2 to 15 %) by weight of hydrophobic or hydrophilic fused silica, ,a bleed inhibitor , and optionally , up to (15 %) by weight of styrene rubber or styrene rubber-styrene block copolymer or semi liquid

rubber. The grease can advantageously be used as a cable filling material, especially for optical fiber cable [92].

A grease composition for use as a cable filling material which contain a bout (25 to 75) parts by weight of castor oil or a ricinoleate polyol, about (13 to 71) parts by weight of a hydroxyl-terminated polymer of polymerized castor oil or the reaction product of a polyisocyanate compound and castor oil or a ricinoleate polyol, and about (4 to 12) part by weight of colloidal particles such as silica, clay, or mixture thereof. Optionally an antioxidant component can be added to impart high temperature resistance, a bleed inhibitor, typically of a rubber component, can be added to improve bleed resistance, a water blocking agent of a super absorbent compound can be added to reduce water transmission, microspheres can be added to reduce the weight of the formulation, and / or conventional additives such as fungicides, bactericides etc. can be included. The invention also relates to an article of manufacture such as cable having a sheath surrounding a plurality of optical fibers therein, with one of the grease compositions of the invention located there in [93].

I-3-2-6-Multi-purpose greases

Multi-purpose greases combine the properties of two or more specialized greases. This permits the use of a single type of grease for a variety of applications. It is possible to replace as many as six specialized greases with single multi-purpose grease and get better results at all the same time. Most of multi-purpose greases have a soap base of barium, lithium, or calcium complex. For example, the lithium soap greases. They are not only water resistant and corrosion inhibiting but they have very good mechanical and oxidation stability.

By reducing the number of lubricants, which company keeps in stock, the lubricator's job becomes much

easier. Another advantage is that it helps reduce the chance of error in application.

Good multi-purpose lubricating greases have to perform well in a number of applications. It should have a high melting point and operate well at continuous temperatures of 250 °F or more. Such grease should also have good resistance to water and exceptional stability [94].

Stankowski, L., et al. prepared a greases consist of poly-α-olefin oil 20-80, ester oil (derived from a dicarboxylic acid) 20-80, lithium 12-hydroxystearate 8-14, lithium azelate 1-3, lithium stearate ≤1.2, dialkylearylamine 0.1-0.6, zinc dialkyle dithio carbamate, Sb dialkyle dithio carbamate, or dialkyle dithio carbamate of an organic molybdenum complex 0.2-1.5, alkyl phenl 0.1-0.3, alkylthioadazole, sulfurized imidazole, or polysulfide (obtained by sulfuration of olefins or esters of unsaturated fatty acids) 0.05-1.5 and low viscosity naphthinic oil ≤ 10.0 wt. %. The lubricating grease is pressure resistance, vibration resistance and suitable for a wide temperature range. The grease also protects aircraft parts against corrosion [95].

I-4-Greases characteristics

Various properties of greases can be determined by means of a laboratory analysis , but the final criterion of its suitability will always be the actual behaviors of the greases in practice laboratory tests as set out in specifications are however useful for identification purposes.

Some of the most important properties of greases in connection with their use will be discussed below : consistency (penetration), dropping point, apparent viscosity, NLGI consistency number, oxidation stability, high temperature, bleeding (migration), flash point, storage stability, water – resistance and dielectric properties.

I-4-1-Consistency, penetration

The most important feature of grease is its rigidity or consistency. A grease that is too stiff may not feed in to areas requiring lubrication, while grease that is too fluid may leak out. A grease consistency is its resistance to deformation by an applied force.

The measure of consistency is called penetration. Penetration depend on whether the consistency has been altered by handling or working. ASTM D27 and D1403 method measure penetration of unworked and worked greases [96].

Grease consistency depends on the type, amount of thickener used and the viscosity of its base oil, even though base oil viscosity affects consistency, it is important to note that a grease can have a high consistency and low base oil viscosity or vice versa [5]

Grease composition containing a poly urea grease thickeners and certain acylated alkylen polyamine are disclosed [97].

I-4-2-NLGI consistency number

The NLGI (National Lubrication Grease institute) has established consistency numbers or grade numbers, ranging from 000 to 6, corresponding to specified ranges of penetration numbers. Table below lists the NLGI grease classification along with a description of the consistency of each classification [98].

NLGI number	ASTM worked penetration 0.1 mm (3.28 × 10°F)	consistency
000	445-475	Semi fluid
00	400-430	Semi fluid
0	355-385	Very soft
1	310-340	Soft
2	265-295	Common grease
3	220-250	Semi hard
4	175-205	Hard
5	130-160	Very hard
6	85-115	Solid

I-4-3-Dropping point

Dropping point is a qualitative property of lubricating grease that gives a general indication of the temperature at which a grease passes from a semi-solid to liquid state under specific test conditions. It is measure of the heat resistance of grease.

Dropping point is used in combination with other test based properties to determine the suitability of grease for specific applications.

Dropping point is applicable to grease that contain soap thickeners. Greases with other thickeners such as many synthetic grease, will not exhibit a change of state. Instead, they separate oil and the dropping point property dose not applies [(95)].

A grease composition of a lithium soap of an epoxy substituted and / or an unsaturated fatty acids exhibiting a relatively high dropping point [(98)].

I-4-4-Apparent viscosity

A Newtonian fluid can be described as a fluid that maintains constant velocity across all shear rates (shear stress varies linearly with shear rate). These fluids are called

Newtonian because they follow the original formula established by Sir Isaac Newton in his low of fluid mechanics. Some fluids, however, don't behave this way. In general, they are called non – Newtonian fluids. A group of non – Newtonian fluids in which its viscosity increase as the shear rate decrease and vise versa as in the case of grease.

Generally speaking, kinematic viscosity (cSt) is related to absolute viscosity (cP) as a function of the fluid's specific gravity (SG) according to the equation [99]:

$$cSt = cP/SG$$

Or the equation inverse

$$cP = cSt \times SG$$

Apparent viscosity, at start - up, grease has a resistance to motion, implying a high viscosity. However as grease is sheared between wearing surfaces and moves faster, its resistance to flow reduces. Its viscosity decrease as the rate of shear increases. By contrast, oil at constant temperature would have the same viscosity at start up as it has when it is moving. To distinguish between the viscosity of oil and greases, the viscosity of grease is referred to as "apparent viscosity".

Apparent viscosity is the viscosity of a grease that holds only for the shear rate and temperature at which the viscosity is determined [96, 100-102].

I-4-5-Oxidation stability

This is the ability of grease to resist a chemical reaction with oxygen. The reaction of grease with oxygen produce insoluble gum, slugs and lacquer like deposits that cause sluggish operation, increased wear and reduction of clearance. Prolonged high-temperature exposure a accelerate oxidation in greases [96].

The oxidation stability of polyester based lithium soap thickened greases is improved by use a synergistic

antioxidant combination comprising a mixture of alkylated diphenylamine and phenol thiazine [103].

I-4-6-High temperature effect

High temperature harms the greases more than it harms oils. Grease, by its nature, can not dissipate heat by convection like circulating oil. Consequently , without the ability to transfer away heat , excessive temperature results in accelerated oxidation or even carbonization where greases hardness or form a crust .effective grease lubrication depends on the greases consistency.

High temperature induces softening and bleeding, causing grease to flow away from needed areas.

The mineral oil in grease can flash, burn or evaporate at temperature above 350°F. High temperature above 73-79 °C can dehydrate certain greases such as calcium soap grease and cause structural break down. The high evaporation and dehydration rates at elevated temperatures require more frequent grease replacement [96, 104, 105].

Shinoki, K. et al. prepared a grease consist of powder mixtures of sodium borate pentahydrate 40-90, sodium carbonate 6-30, fatty acid sodium or calcium salt 5-30 and sodium molybdenum oxide 1-30 wt.% The component is useful for hot rolling seamless steel pipes [106].

I-4-7-Low temperature effect

If the temperature of the grease is lowered enough. It will become so viscous that it can be classified as a hard grease. Pumpability suffers and machinery operation may become impossible due to torque limitations and power requirements [20-22].

I-4-8-Bleeding (migration, syneresis)

Bleeding is a condition when the liquid lubricant separates from the thickener. It is induced by high temperature and also occurring during long storage periods.

Migration is a form of bleeding that occurs when oil in grease migrates out of the thickener network under certain circumstances. As the oil separates from the grease, thickener concentration increases and plugging gets worse.

Syneresis is a special form of bleeding caused by rearrangement of the structure due to physical or chemical changes in the thickener [107-109].

I-4-9-Flash Point

The flash point is the lowest temperature, to which a lubricant must be heated before its vapor, when mixed with air, will ignite but not continue to burn. The flash point is useful in determining a lubricant volatility and fire resistance [96, 110].

I-4-10-Storage Stability

Most lubricating oils and greases deteriorate with time. However good storage practices promote sufficient stock turn over so that lubricants are used before performance loss occurs. The storage environment greatly affects the shelf life of lubricants and greases. High heat (greater than 45°C) and extreme cold (less than - 20°C) can effect lubricant stability. Heat increases the rate of oil oxidation, which can lead to deposit formation and the viscosity increase. Cold temperatures can cause wax and possible sediment formation. Exposure to light can change the color and appearance of lubricants. To prevent this change, keep lubricant in their original metal or plastic containers .Some lubricant additive may react with water, forming insoluble matter. Water may also promote

microbial growth at the oil / water interface. Store lubricant in a dry location, preferably indoors [96].

A fluorine containing grease comprising polytetrafluro ethylene and a perfluro alkyl polyether has good homogeneity storage stability [111].

I-4-11-Water – resistance

The resistance of a grease to water contamination is an important property where water will be present to a greater or less extent. The presence of water cause changes of grease consistency, emulsification with water soluble soap grease and a reduction in mechanical stability.

The mount of grease washed out in one hour is a measure of resistance of product to water washout. Greases which repeal water are suitable for preventing the formation of a continuous conductive layer on a greasy or oily surface, but remain in drops which are electrically insulated from each other. Greases coating on insulators have been successful in preventing flash over in extremely contaminating conditions [96, 112, 113]

I-4-12-Pumpability

Pumpability is the ability of a grease to be pumped or pushed through a system. More practically, Pumpability is the ease with which pressurized grease can flow through lines [20-22].

I-4-13-Dielectric Properties

The basic electrical properties of dielectrics are volume resistivity, electronic strength (dielectronic break down strength), permittivity or dielectric constant and dielectric loss. The choice of dielectric for each particular purpose is determined by the temperature and electrical field frequency dependencies of these quantities.

Volume resistivity or its reciprocal, volume conductivity, depend on the presence of free charges (electrons or ions) and their mobility. A dielectric usually contains very few free charges, and therefore has a low conductivity (of the order of 10^{-19} to 10^{-13} $ohm^{-1}.cm^{-1}$) with rising the temperature the conductivity of dielectric increases owing to increasing mobility of the free charges.

The permativity or dielectric constant of a substance (ε') is defined as a ratio of the capacity of an electric capacitor filled with the substance to that of the same capacitor in vacuum, at definite external field frequency.

Dielectric loss is the part of the energy of an electric field that is dissipated irrecoverably as heat in the dielectric. Dielectric loss is characterized by the loss factor $\varepsilon'' = \varepsilon' \tan \delta$ [114-115].

I-5-Functional properties of greases

I-5-1-Advantages of greases

1) Functional as a sealant to minimize leakage and to keep out containers. Because of its consistency, grease act as a sealant to prevent lubricant leakage and also to prevent entrance of corrosive contaminants and forging materials. It also acts to keep deteriorated seals effective (where as an oil would simply seep away).

2) Easier to contain than oil. Oil lubricant can require an expensive system of circulating equipment and complex retention devices. In comprise grease; by virtual its rigidity is easily confined with simplified, less costly retention devices.

3) Holds solid lubricants in suspension. Finally ground solid lubricant, such as molybdenum disulfide and graphite, are mixed with grease in high temperature service (over 315°C) or in extreme pressure applications. Grease holds solid in suspension while solids will settle out of oils.

4) Fluid level dose not have to be controlled and monitored [116].

I-5-2-Notable disadvantages of greases

1) Poor cooling. Due to its consistency, grease cannot dissipate heat by convention like circulating oil.

2) Resistance to motion. Grease has more resistance to motion at start up than oil, so it is not appropriate for low torque / high speed operation.

3) More difficult to handle than oil for dispersing, draining, and refilling. Also exact amount of lubricant can not be as easily metered.

4) Softening during storage.

5) Surface discoloration/ upon long storage some light-colored lubricating greases may become orange or red colored on the surface, this indicates that oxidation has started.

6) Excessive oil separation.

7) Aeration, if air becomes entrapped during manufacture and is not removed after words, it may be present as very fine bubble while will makes the product lighter in color and in weight than normal.

8) Age hardening, this is more evident on the surface of a container where the product will be much stiffer than the body of the lubricant [112].

I-6-Applications of greases

Greases and oil are not interchangeable. Grease is used when it is not practical or convenient to use oil. The lubricant choice for specific application is determine by matching the machinery or design and operating conditions with desired lubricant characteristics. Grease is generally used for:

1) Machinery that runs intermittently or is in storage for an extended period of time. Because grease remains in place, a lubricating film can instantly form.

2) Machinery that is not easily accessible for frequent lubrication. High quality greases can lubricant isolated or relatively inaccessible components for extended periods of time without frequent replenishing. These greases are also used in sealed for life applications such as some electrical motors and gear boxes.

3) Machinery operating under extreme pressure conditions such as high temperature and pressures, shock loads, or slow speed under heavy load. Under these circumstances and adequately lubricant, Where as oil film can be too thin and can rupture.

4) Worn components. Grease maintains thicker films in clearance enlarged by wear and can extend the life of worn parts that were previously oil lubricated. Thicker grease films also provide noise insulation.

5) Dielectric grease also provides oxidation and heat stability, and can withstand a wide temperature range without breaking down. Dielectric grease is used to dissipate heat from some electronic component, and is also useful in lubricating machines such as slide contact switches and relay contacts. It is used in electrical transformers also can include other components to enhance the life and function of the transformer oil.

6) Organic hydrocarbon grease including rubber or resin or waxes are very wildly distributed through at industrial branches they are used in electrical systems and electronic equipments to seal connectors, plug and sockets to pot cob transformers and capacitors , cables , and to prevent electrical leakage [117-120].