Chapter 1: Introduction

Since the great majority of conventional pesticides are imported as ready to use formulations. Therefore, efforts should be directed towards using the local raw materials and products in the formulation of different types of pesticides. Establishing the industry of formulation of pesticides in its sense by utilization the local basic ingredients would contribute to the national income of Arab Republic of Egypt. Moreover, pesticide formulations with reasonable price would be introduced and marketed with a consequence decrease in pest control costs.

I- The necessity of formulations

Pesticides are in general used at extremely small dosage per acre. In order that they may do their job efficiently they must be distributed as evenly as possible. It customary to use some form of diluents or bulking agent through which the chemical is evenly distributed which is itself then applied at much higher volume. The cheapest bulking agents in most areas undoubtedly water, also the petroleum oils are often used [1].

The use of surfactants and certain additives in pesticide formulations would improve their field performance and increase the bioactivity with consequent decrease in their rates of application, then reducing plant protection costs, there by, approaching close to the principle of integrated pest management (IPM) by reducing the hazard to the environment[2].

The wide variety of agrochemical formulations, which is available, requires a range of different formulation additives to produce safe and usable products. The most important formulations additives are surface active agents.

The surfactants often determines the maximum concentration of the formulation that can be achieved, the particle or droplet size, long term stability and some times even the biological activity of the formulation [3].

Agrochemicals products have been used widely for many years to increase the yields and improve the quality of food and fiber crops and to improve public health all over the world. The agrochemical industry has become a major business producing products with a total world sales value estimated in 1997 at over U.S. $30 billion, and it plays an important role in the economies of most countries. The agrochemical business represents a significant opportunity for surfactants and other essential formulations additives as well as adjuvant for spray application [4].

Pest control represents a critical factor and highly productive inputs for increasing crop yields and preventing crop losses before and after harvest. Till now chemical control has a main role in pest control programmers in all developing countries. The great majority of pesticides employed in Egypt are used to protect cotton which is still the cash crop for exportation. The often and indiscriminate use of pesticides has led to several adverse consequences and the environmental quality has been deteriorated to a great extent.

Active ingredient of pesticides will often have to be modified to allow for field use these modifications may include adding inert ingredients such as solvents, wetting agents, emulsifiers, carriers and diluents to the pesticides. This will result in different formulations. Some examples of the different type most common formulations include wettable powders (WP) which are made from solid active ingredients with high melting points which are suitable for dry grinding, granular formulations (GR) are used for direct broad costing to the field as pre-emergence herbicides or as soil insecticides, solution concentrate (SL), are aqueous solutions of active ingredients which mainly require dilution in the spray tank. Some solution concentrate formulations contain a surfactant, often a non – ionic ethylene oxide condensate, to assist wetting onto the leaf surface, emulsifiable concentrates for oil-soluble solids, and granules and seed treatments for direct application [5].

Pesticidal active ingredients encompass abroad range of chemicals, each with its unique chemical and physical properties and made of action. The main categories of pesticides are insecticides, fungicides, herbicides, rodenticides, nematicides, mollusicides and acaricides [6].

Pesticidal active ingredient or toxicant is the part of formulated product that is principally responsible for pesticidal effects as preventing, destroying, repelling or mitigation insects, fungi, weeds, rodents, etc. The formulation for a product depends on many factors. The physico- chemical properties of an active ingredient, such as melting point, solubility, sensitivity to light, tendency to reduction or oxidation, crystallization properties and etc. [7].

The inert ingredient or supplements are inactive ingredient that have no pesticide action but acts as wetting agents, dispersing agents, emulsifiers, spray adjuvant, solvents, carrier/ diluents, etc. [8].

The most important formulations are those which are made for dilution into water in a spray tank. In these cases the choice of formulations additives is very important to ensure that the product mixed and diluted easily [9].

II-The major types of formulation and their international code

The most common formulations are still soluble concentrates for water-soluble chemicals, emulsifiable concentrates for oil-soluble chemicals, and wettable powders and suspension concentrates for insoluble solids. Granules and seed treatments for direct application have also been produced for many years. In recent years the number of formulation types has increased enormously to meet the needs of operator and environmental safety or to improve the activity and persistence of the active ingredient. An international coding system was, therefore, devised by GIFAP in 1984 (in 1996 GIFAP was renamed GCPF - Global Crop Protection Federation, based in Brussels, Belgium. This organization is now known as CropLife International listing about 80 different types of formulation. The major types of formulations and international codes are shown below:

Formulations	**GIFAB Code**
Granules	GR
Wettable Powder	WP
Soluble liquid	SL
Emulsifiable concentrate	EC
Suspension concentrate	SC
Soluble powder	SP
O/W emulsions	EW
Suspoemulsions	SE

Micro emulsions	ME
Water – dispersible granules	WG
Microcapsules	CS

There are five main types of pesticides to formulate. They may be classified according to their solubility properties:

1- Soluble in water to 30-40% and soluble in solutions.

2- Soluble in water but unstable.

3- Partially soluble in water.

4- Insoluble in water but soluble in oils.

5- Insoluble in all solvents without decomposition.

Group 1:

There are simply formulated as soluble powder or solution concentrates.

Group 2:

These, if readily soluble, may be granulated for case of handling dissolved on the spot.

Group 3:

These chemicals are most easily formulated as stock solutions in a solvent, which is miscible with water, and then on dilution to the spray solution the chemical below its solubility limit, dissolves completely.

Group 4:

These chemicals were formulated as emulsifiable concentrates

Group 5:

These chemicals were formulated as wettable powder or flowable formulation.

III- Formulation objectives

The main objectives of formulation can be summarized as follows:

To provide the user with a convenient, safe product which will not deteriorate over a period of time, and to obtain the maximum activity inherent in the active ingredient.

Formulators need to take into account a number of interacting in the choice of the specific formulation type for each active ingredient. The main factors govering the choice of formulations are:

1- Physico-chemical properties.
2- Biological activity and mode of action.
3- Method of application.
4- Safety in use.
5- Formulation costs.
6- Market preference.

Once these parameters have been determined, proper selection can be made of the final formulation type and the use of inert ingredients including surfactants and other additives to produce a stable formulation with at least a 2 year shelf life during storage under varying climatic conditions [9].

The aims of the present research are

1- Determination physico- chemical properties of some commercial conventional pesticides: insecticides, fungicide and herbicide, also, determination the physico-chemical properties of its spray solution at field dilution rate.

2- Local preparation of the studied commercial conventional pesticides using local raw materials and products and determination both their physico-chemical properties and physico-chemical properties of their spray solution at field dilution rate.

3- Determination the pesticidal efficiency of both commercial and locally formulated convention pesticides against pests infested different crops.

4- Determination of the deposit and residues of sprayed commercial and locally formulated pesticides on treated crops.

1-1- Emulsifiable concentrates (EC)

Emulsifiable concentrates (EC) have been very popular for many years and represent the biggest part of all pesticide formulations in terms of consumption. Emulsifiable concentrates are made from oily active ingredients or from low melting, waxy, solid active ingredients, which are soluble in non-polar hydrocarbon solvents. Surfactant emulsifiers are good emulsion stability properties in the spray tank. Careful selection of a balanced pair emulsifier bland is frequently necessary to ensure emulsion dilution stability is maintained over widely differing climatic conditions and degrees of water hardness. The formulation of emulsifiable concentrates has been greatly facilitated by the non – ionic surfactants such as nonylphenol hydrophobic chain condensed with 12 or more moles of ethylene oxides. The other component of the balanced pair is generally anionic surfactants such as oil soluble calcium salt of dodecylbenzene sulphonic acid [9].

Emulsifiable concentrates containing toxic agents are usually formulated with blends of anionic and nonionic surface active agents such as alkyl sulfonates and alkyl aryl polyglycolehter condensates. Also, they investigated the properties of emulsifiable concentrates of toxaphene and diazinon dissolved in kerosene and xylene using surfactant blends of calcium dodecyle benzene sulfonate (CODBS), 70%, and a series of nonylphenol elhoxylate [10].

The most insecticidal emulsifiable concentrate, containing the mixtures of nonionic surfactants such as the polyglycol etheres, and anionic surfactants which include dodecyl benzene [11].

The mixtures of anionic/ nonionic emulsifiers blended together were most efficient for the preparation of emulsifiable concentrates, due to the synergistic effect of mixture of the two types [12].

1-1-1- Choice of suitable solvent

The choice of solvent depends on the toxicant solubility, especially at low temperature the solvent should have a moderately high flash point and a low order of phytotoxicity or irritation and it should be low cost and plentiful in supply. As a general rule, the dissolving power of the solvent increase as it aromaticity increases [13].

Choice of solvent is based on physical properties such as salvation power for the active ingredient, low phytotoxicity to crops, does not react with the active ingredient or emulsifier, flash point of formulation will generally be higher than the lowest flash point of the component, ready availability and low cost. Solvent – based formulation are generally preferred for foliar – applied pesticides, as they tend to enhance uptake and translocation via penetration, cuticular solubilization and stomatal entry [14, 15].

The first main groups of solvents are aliphatic paraffins, which are characterized by very low solubility in water poor solvent power, low toxicity and low phytotoxicity. The second main group and the most common comprise the aromatic solvent such as xylene.

1-1-3-Co-Solvent

Sometimes even aromatic solvents are too poor to dissolve a sufficient percentage of a pesticide suitable for practical application in the case with lindane, in such case auxiliary or co-solvent usually ketonic in structure, are added to formulation to improve solvency [13].

Co-Solvents are used to prevent crystallization of active ingrediens when the formulation is emulsified in water. Certain ketons are useful for emulsifiable concentrate formulations because they are powerful solvents. However, they are fairly polar and may be reactive, and also have some water solubility. The most popular members of this group are cyclohexanon; methyl cyclohexanone, isophorone, acetophenone and N-methyl pyrollidine. Co-solvents may be necessary to optimize solubility and stability [16].

1-1-4 Emulsifiers and theories of emulsification

An emulsifying agent can be defined as a substance, which stabilizes a suspension of droplets of one liquid in another liquid phase, without the emulsifying agent, the two liquids would separate into two immiscible liquid phases. Therefore, it is an essential ingredient in the formulation of liquid oily. Active ingredients and solvents, which need to be emulsified into water in the spray tank [17].

The introduction of EC began with chlorinated hydrocarbon pesticides. They began using of anionic surface active agents of fatty acid salts as the common soap [17].

Water oil emulsifiers should have an HLB 3 to 6, for wetting agent an HLB 7 to 9, for oil in water emulsification an HLB 10 to 15, and for solubilization an HLB of 15 to 18 [18].

The excellent solvent and surfactant could improve the penetration and distribution of the toxicant. It must be avoided to use solvents and emulsifiers which may physically reduce the penetration ability of the toxicant [19].

The polar toxicant required more polar (more hydrophilic) emulsifier system [20].

The kinetic of formulation of emulsion is still not fully known since it depends on the rates of surfactant diffusion to interface will be very complicated, for a blend of surfactants of different molecular weights and charge on the interface and the electrical potential. The lower molecular weight nonionic material will diffuse fast to the interface to be later displaced competitively by the slower diffusing of higher ethoxylated surfactants, which are more hydrophilic – such multicomponent emulsifiers will provide a better packing of the interface and give better, more stable emulsion [21].

Critical Micelle concentration (CMC) is of fundamental importance in the selection of surfactants for specific application. In general, surface activity is due to non- micellar surfactant and the micelle act as a reservoir for the unassociated surfactant molecules and ions. At concentration greater than CMC value, the surface tension of the solution does not decrease further with an increase in surfactant concentration. Often detergency and foaming at their highest at the CMC [21].

The ability of surfactant solutions to dissolve or solubilize water insoluble material starts at CMC and increase with the concentration of micelles.

The spatial requirements of water molecules hydrogen bonded to the ether oxygen's of the nonionic ethoxylated surfactants will prevent them from packing closely on the oil – water interface. On the other hand, the ionic surfactants charged head will be affected by columbic repulsion and thus prevented fro packing closely on the interface. Blending the two systems in the emulsifier will to an extent, overcome this handicap, improving surface packing for a better stabilization of emulsion with less emulsifier. The anionic surfactants in the blends add charge to the emulsion droplet, preventing coagulation by columbic repulsion, but give a narrow stern layer sphere (4 to 10 A°) with little solvation in the ions with water molecules. The added anionic ethoxylated surfactants protrude much further into the water phase (30-40 A °C) and form a big salvation sphere. The plane of the sphere shear that determines the stern layer is in this way extended and stabilized by the hydrated ethylene oxide chain, resulting in improving emulsion stability [22].

For oil in water system, emulsifier that are not sufficiently hydrophilic for the required conditions will not sufficiently stabilize the emulsion droplets. The emulsion goes through the stage collapsing into bigger droplets, a rapid sedimentation coalescence (oiling). Emulsifiers that one to hydrophilic for the specific conditions will stabilize the emulsion droplets, but they will come close enough to cause interlocking of accordingly a slight increase in the rate of sedimentation (creaming) over the optimum blend [22].

The mechanism of forming emulsion, are reduction of the interfacial tension, forming a rigid interfacial film, and electrical charge [23].

An emulsion may become unstable due to a number of different types of physical and chemical properties. Physical instability results in an alteration in the spatial distribution or structural organization of the molecules, whereas chemical instability results in an alteration in the chemical structure of the molecules creaming, flocculation, coalescence, partial coalescence and phase inversion are examples of physical instability [24].

The term stability usually refers to the ability of an emulsion to resist changes in its properties over time: The more stable the emulsion, the more slowly it is properties change [25].

The most stable emulsion of oil/ water types are formed when there are two emulsifying agents presents, one of which is primary an oil soluble (O/W) emulsion and other a water soluble (W/O emulsion). So, the oil soluble surfactant, which generally has a long straight hydrophobic group and a hydrophilic head that is only slightly polar increases the lateral interaction between the surfactant molecules in the interfacial film and condenses it to one that is mechanically stronger than in its absence [4].

The total concentration of the emulsifier blend is usually 5-10% of the formulation. There are no definite rules to determine the ratio of anionic to nonionic surfactant in the mixed emulsifier, but guidance can be obtained from HLB system. HLB stands for hydrophile-lipophile balance and the higher the HLB the more hydrophilic (water – soluble) is the surfactant. The HLB range 8-18 will normally provide good oil – in – water emulsions. The optimum ratio of anionic and nonionic surfactants is determined experimentally to give spontaneous emulsification in water, and to give a stable emulsion with very little creaming and oil droplet coalescence [9].

1-1-5-Specification and optimum characteristics of Emulsifiable concentrate

The emulsifiable concentrate should show good emulsion characteristics such as spontaneity, emulsion stability, re-emulsification and performance in various water hardness. He added that in the successful emulsifable concentrate, the pesticides and emulsion should be stable under both low and high temperature conditions, the concentrate should be compatible with other formulations with which it is likely to be encounted [13].

Dilution rate, water hardness, agitation, amount of emulsifiers and temperature all have their effect on results of laboratory tests[25]. Most field situations require emulsifiable insecticide concentrates that exhibit spontaneity of emulsion and subsequent emulstion stability especially for use n sprays no equipped with agitators [26].

Various specifications for emulsifiable concentrate to conform to different conditions. The emulsifiable concentrate should not show any solid or oily separation when it cooled at 0°C for seven days. Its flash point should not be lower than 22.8°C (73°F). The emulsion should not show any oil separation and the creamy separation or precipitation should not exceed than 2 ml when it emulsified with hard and soft water at the rate of 5%. The foam should not exceed than 60 ml after one minute at field dilution rate. The free acidity or alkalinity should be in a range from 0.1 to 0.3%. The emulsifiable concentrate subjected to tropical storage at 54°C for 14 days should be chemically and physically stable. The tropical storage tests ensure that the emulsifiable concentrates which pass this test will have a reasonable life under different storage conditions [27, 28].

1-1-6- Locally prepared emulsifiable concentrate in Egypt

Suez Sol. A (a high aromatic local solvent) had been used with three local emulsifiers one anionic, Emulgator A, and two nonionic Emulgator B and Hamadol 78 For preparing successful E.C of a number of chlorinated hydro carbons, Organic phosphates alone and in mixtures [29].

The physico-chemical characteristics of the successful E.C was studied to find:

1- The successful E. C which had passed the emulsion test, proved also to be stable on cold and tropical storages except for the few formulations of high free acidity which was caused by Emulgator A, the high acidic emulsifier.

2- Specific gravity and viscosity can be used for predicting the type of creaming and the degree of spontaneous emulsification of E. C.

3- It was found necessary to measure surface tension at the field dilution to predict the field wettability. The leaves could be easily wetted by spray liquid through the reduction of surface tension for increasing the spreading properties of droplets.

4- It was also recommended that emulsion stability test must be alone at field concentration [30].

Locally emulsifying agents which were three anionic surfactants (Emulgator A., Nestaboon and Sodium paste) and five nonionic (Emulgator B, Emulgator NS, Emulgator A. O., Egyptol BL 25% and Egyptol BIM) were evaluated to use for preparing successful insecticide EC of lindane 20%, malathion 57% and methyl parathion 50% [31].

Five locally emulsifieble concentrates prepared by using sulfonated mineral oil, malathion and amine salt of 2, 4-D as active ingredient, where one anionic emulsifier (Sodium paste) and two emulsifiers (Emulgator NS and Egyptol BIM) were used preparing these EC's with xylene as a solvent [32].

Some successively emulsifiable concentrates prepared by using some plant oil (fixed oils) as linseed oil, cottonseed oil, corn oil, sesame oil and castor oil as active ingredients with dissolving these plant oils in xylene and using some emulsifies as PEG 200 ML, PEG 200 DL, PEG 200 MO, Nastabon and Hamadol A/ 600. These successful EC'S were evaluated against cabbage aphids and mature stages of whitefly [33].

Successful insecticides EC of cypermethrin 25% and esfenvalerate 5% were prepared by using surfactants as Tween 85, Nonylphenol ethoxylate, Castor oil sulfonate, Atlox 3335 and Atlox 3387. Evaluation the insecticidal efficiency of these successful EC's against the 4th instar larvae of cotton leaf worm [34].

Some plant oils: Cottonseed oil, Citronella oil and Camphor oil as EC were prepared using suitable solvents (e.g. xylene and isopropyl alcohol) and suitable emulsifiers (e.g. PEG 600 DO, tween 80 and tween 20) at different concentrations and evaluated the molluscicidal affects these emulsifiable concentrates against the small land snail *Helicella vestalis* [35].

1-2- Wettable powder (WP)

Wettable powder formulations of pesticides have been known for many years and are made usually from solid active ingredients with high melting points which are suitable for dry grinding through a mechanical grinder such as a hammer or pin type mill or by air milling with a fluid energy micronizer. Air milling gives much finer particles (5–10 microns) than mechanical milling (20–40 microns) and can also be more suitable for active ingredients with lower melting points. However, care must be taken to prevent, suppress or contain dust explosions which may occur if a source of ignition, such as static energy, is present in both types of mills. Wettable powders usually contain dry surfactants as powder wetting and dispersing agents and inert carriers or fillers. They frequently contain more than 50% active ingredient and the upper limit is usually determined by the amount of inert material such as silica required to prevent the active ingredient particles fusing together during processing in the dry grinding mills [9].

1-2-1- Pesticides

Pesticides suitable for preparing wettable powder formulations should pass certain properties:

- Active ingredients should have high melting points.
- The active ingredients must not react with water when they diluted during application and also it must not dissolve in water.
- For toxicants with particle sizes in excess of 300 microns it is advisable to pre-grinded those to less than 50 microns [36].

1-2-2- Surfactants

a- As suspending agent

The suspensions is thermodynamically unstable this is in view of high surface area created in their preparation, which normally accompanied by large surface free energy.

The system tends to reduce this energy by number of break down process so the particles will be aggregated. This aggregation is usually prevented by use of powerful suspending agent or dispersing agent such as block or graft copolymers and ionic or nonionic surfactants [37].

b- As wetting agent

A wetting agent can be defined as a substance which added to liquid for increasing the wetting and spreading of the treated surface with the liquid by reducing the interfacial tension between the liquid and the surface which speeding on it.

The contact angle between the liquid droplet and the surface is reduced until, the contact angle reaches zero and complete wetting will take place. Therefore wetting agents are used for two main functions in agrochemical formulation.

- During processing and manufacture to increase the rate of powders into water or make concentrates for soluble liquids or suspension concentrates.
- During mixing of the product with water in spray tank to reduce the wetting time of wettable powders and to improve the penetration of water – dispersible granules [3].

The wetting agent lower the interfacial tension between the solid particles and water to ensure that the powder (toxicants) wets and mixes with water in spray tank easily (e.g.) aliphatic alcohol ethoxylates, sodium laurayl sulfates and nonylphenol ethoxylate [4].

C- As dispersing agent

It is necessary to prevent the particles in the spray tank from flocculating or aggregating together and ensure that particles remain suspended during the spraying operations (e.g.). A popular dispersing agent is a lignin sulphonate which acts by changing the electrical charge on dispersed particles [38].

The amount of surfactants should be sufficient in wettable powder to wet the target surface, the percentage of surfactants in wettable powder formulations 1-5% [28].

1-2-3- Selection of the suitable carriers

The insecticides dust diluents and carriers classified into two major groups, i.e. botanical flour and mineral products. Botanical flour group includes tobacco, walnut shells, wheat and wood flours. The mineral group consists of elements, oxides, carbonates, sulfates, Silicates and phosphates [39].

The main physical properties of the diluents are as follows: Particle shape, density, particle size, hardness, electrostatic charge, absorption, adsorption, chemical nature of the particles, bulk density and sticking properties [40].

The sorptive capacity of diluents or carriers affects the caking of insecticides and hence their quality in storage. The diluents which have a high sorptive capacity as the diatomaceous earth is usually used as primary carrier for formulating the liquid insecticides as dust concentrate or master mixes. In general, the sorptive diluents or carriers can be formulated with solid insecticides in any proportion [41].

The stabilization of dry pesticides formulations and the product instability was generally assumed to be caused by several factors such as pH, catalytic amount of heavy metal impurities, moisture, air (oxygen), light, temperature, etc. Product decomposition could be attributing to one or more of these factors [42].

The surface acidity of a variety of solid catalyst surfaces was measured by using appropriate indicates (Hammett indicators) [43].

Many of the active ingredients are easily decomposed by the diluents or carriers. The rate of decomposition varies a great deal according to the type of carriers where, talcs and kaolinites offer few problems than other types of inerts. The efficiency of solid formulations depends on the particles size and content of active ingredient. The active ingredient after a given time may be decreased to a great extent if an inert having no catalytic activity is being used. The tests of pH values, humidity and hygroscopicity are necessary to determine the probable catalytic activity of inert or carriers. Also, when an inert has a neutral pH, but a lot of acidic sites, it will logically also has a lot of alkaline sites and will decompose all types of pesticides which are sensitive to either acid or base. The pH is the average of the acidic and alkaline sites, which do not neutralize each other in the solid state, and do not change the color of indicator [44].

The influence of different carriers on the physical and biological stability of Bacu/virus anticarsia wettable powder formulations was studied. The carriers in these formulation are amorphous silica, attapuligite and kaolinite all formulations except kaolinite, maintained the physical parameters required of good wettable powder. Kaolinite showed reduction in wettabillity [45].

Amount of inert material, such as silica, may be required to prevent the active ingredients particle fusing together during processing in the dry grinding mills interfillers such as talc or kaolin is also needed to prevent the formulated product from caking or aggregating storage [4].

1-2-5 Specifications of wettable powder formulations

1- Active ingredients should remain suspension in 30 minutes. An acceptable pesticide wettable powder should pass the suspensibility test to have more than 60% of suspensibility in soft and hard water [28].

2- The foam should not exceed than 60 ml after one minute at field dilution rate [46].

3- The free acidity or alkalinity should not exceed 0.1 to 0.3 % [27].

4- The bulk density of the powder after compacting (packed bulk density) shouldn't exceed than 60% from that before compacting [46].

5- 98% of pesticide (powder) should pass through a 75 microns using wet sieve screen analysis [46].

6- The wettable powder subjected tropical storage at 54°C for 14 days should be chemically and physically stable. The tropical storage test ensures that the wettable powders which pass this test will have a reasonable life under different storage conditions [46].

1-2-6- Locally prepared wettable powder in Egypt

Bacillus thuringiensis is the most widely used biopesticides among many methods available to control insects. It was prepared as spray dried wettable powder formulation containing 10% wt.wt. *B. thuringiensis*, 10% wt./wt gelatinized tapioca starch, 10% wt./ wt. sucrose, 38% wt./ wt. tapioca starch, 10% silica fume, 2% polyvinyl alcohol, 5% v./v. Tween 20 (surfactant) and 1% v./v. antifoam . This formulation had 65% suspensibility, 24 sec. for wetting time and 5.6 x 10^4 CFU/ ml of LC_{50} value against *Spodoptera Exigne* larvae [47].

An organic acid salts (calcium oxalate) prepared as two successful wettable powder formulations in concentrations 95% by using mixture between locally prepared anionic and non – anionic surfactants, where surfactants in WP1 are [Potassium laurate (3%)] + PEG 600 ML (2%)] and surfactants in WP2 [Potassium laurate (2.5%) + PEG400 Dipalmitat (2.5%) + PEG 400 Dipalmitate (2.5%)] , which proved pesticidal efficinency against cotton leafworm insects infested cotton plant and alternari-alternate fungus infested tomato [48].

1-3- Soluble powder (SP)

It is one of the simplest formulations the pesticide which can be formulated, is limited by solubility and hydrolytic (FAO/WHO, 2002), and consist of homogenous mixture in form of powder which makes true solution when applied in water [49].

1-3-1- Surfactants

Surfactant applied in soluble powder will be reduced the surface tension of spray droplet, which is spread on the leaf surface providing more coverage for toxicant by contact angle of spray drops on solid surface, also the surfactants which used in SP formulation should have HLB > 13 and must be soluble in water to avoid any emulsion in the spray solution [50].

The percentage of wetting agents in soluble powder formulation 3-10%, also the wetting agent is applied to optimize biological activity of the pesticide. The welting agent used in soluble powder formulation such as ethylene oxide condensate [28].

1-3-2 Specifications of soluble powder formulation

1- No any precipitation or flocculating should be occurred when SP diluted with water at field application rate [46].

2- The foam at field dilution rate should not exceed than 60 ml after 1 minute [46].

3- The free acidity or alkalinity should not exceed 0.1 to 0.3 % [27].

4- The bulk density of the powder after compacting (packed bulk density) shouldn't exceed than 60% from that before compacting [46].

5- The moisture of SP should not exceed than 2% [28].

6- The soluble powder subjected to tropical storage at 54°C for 14 days should be chemically and physically stable. The tropical storage test ensures that the soluble powders which pass this test will have a reasonable life under different storage conditions [46].

1-3-3-Locally prepared soluble powder in Egypt

Organic acid salts have toxic moiety and are soluble in water as Na-tartarate, Cu-acetate and Na-oxalate are chosen and made as soluble powder formulations in concentration 90%, which mixed with anionic surfactant as potassium laurate (10%) and evaluate the pesticidal efficiency for these SP formulations against cotton leafworm insects and *alternari alternate* fungus [48].

Citric acid and alum (potassium sulfate) were prepared as 90% soluble powder (SP) formulations and adding surfactants (Tween 80 and Tween 20) in concentration 10% to active ingredient. The prepared formulation passed successfully all physico- chemical properties for soluble powder formulation and tested against the second stage of Rootknot nematode [51].

1-4- Soluble Liquid (SL)

The simplest of all formulations to make is the solution concentrate, an aqueous solution of the active ingredient which merely requires dilution in the spray tank. The number of pesticides which can be formulated in this way is limited by water solubility and hydrolytic stability of the active ingredient.

Some solution concentrate formulations contain a surfactant, usually a non- ionic ethylene oxide condensate, to assist wetting on to the leaf surface. Solution concentrate formulations are usually very stable and therefore present few storage problems. Some problems do occur occasionally, such as precipitation during dilution and corrosion of metal containers or spray applicators. However, these problems can be overcome by the use of suitable additives, such as co-solvents and corrosion inhibitors [9].

A typical solution concentrate formulation is shown blower:

Constituents	% w./w.
Active ingredient	20-50
Welting agent	3-10
Anti-freeze	5-10
Water	To 100
Water – miscible solvent	

Nonylphenol or tallow amine ethoxylates are often used as tank mix welters for solution concentrate formulations to enhance bioefficacy. Alternatively, the wetting agent may be built into the formulation to ensure that the correct rate of wetting agent is applied to optimize biological activity. This is often the case, for example, with paraquat and glyphosate formulations. A considerable amount of work is being carried out on – new surfactant wetting agents for glyphosate formulations. In some cases preservatives may be necessary to prevent mould growth or bacterial spoilage during long term storage [52].

Azadirachta indicate extracts prepared as soluble liquid formulation (SL) after extraction by suitable organic solvents (methanol and ethanol) with leaves and seeds. So, each of ethanol extract of seeds, ethanol extract of leaves, methanol extract of seeds and methanol extract of leaves was prepared as (SL) using suitable solvent (e.g. dimethyl formamide) and suitable welting and spreading agent (Tween 80) at suitable and applied concentrations. The molluscicidal effects of the soluble liquids were evaluated against the small land snail *(Helicalla vestalis*) [35].

1-4-1-Specifications for soluble liquid formulations

1- No any precipitation or flocculating should be occurred when SL diluted with water at field application rate [46].

2- The foam at the field dilution rate should not exceed than 60 ml after 1 minute [46].

3- The soluble liquid subjected to tropical storage at 54°C for 14 days should be chemically and physically stable. The tropical storage test ensures that the soluble liquids which pass this test will have a reasonable life under different storage conditions [46].

4- The cold storage for SL at 0 °C for 7 days should have no separation or sedimentation in their formulations after end time of storage [46].

1-6- Correlation between the physico-chemical properties of the spray solution, retention, deposit and pesticidal efficiency

1-6-1- Surface tension of spray solution

As a result of using surfactants as emulsifier, suspending and dispersing agents and as a wetting and spreading agents, therefore, it decreased the surface tension of spray solution and gives the following effects:

The deposition of active materials on foliage is greater from coarse than from fine emulsions, therefore, it became highly describe to develop simple laboratory tests for predicting with reasonable accruing the comparative retention of active materials from spray emulsions on foliage before conducting extensive field trails [53].

The reduction of the surface tension of the pesticidal spray solution would increase its wettability and spreading on the treated surface, then increase insecticidal activity [21].

The use of surfactants in spray liquids reduced both advancing and receding contact angles of the spray on the plant leaves surface, and the retention of insecticides was increased. Surfactants increased penetration of pesticides, resulting in greater activity. This may be attributed to its interaction with pesticides, changing the surface chemical properties of spray solution and / or affect the physical nature of the plant itself [54, 55].

The efficiency of spray application may be assessed in terms of several physical properties, e.g. the retention of spray and the deposition of active material onto the target surface. It is a well known fact that, in agricultural sprays, the emulsion formed should not be too stable to avoid runoff from the surface of the leaves. The impaction of spray droplets is a factor which influences the formation of spray deposits [56, 57].

Surfactants might influence the activity of pesticidal or agricultural chemical sprays at one or more several sites, as follows: (1) within the formulation or spray solution, emulsion or suspension, (2) on the cuticle surface, (3) with in the cuticular layer, (4) within or on the surface membranes of living cells underlying the cuticle, (5) within the plant tissues removed from the treated area [58].

Surfactants have a major significance for improving the physical properties of working solution of pesticides. They facilitate better covering and retaining of the solution on plants with poorly wettable leaf surfaces because they lower the surface tension. Also, the surfactants increase the viscosity of a solution and reduce the evaporation of the drops [59].

Commercial and laboratory prepared insecticide emulsifiable concentrates were tested in the laboratory and in the field to study their physical and chemical characteristics distribution of spray emulsion and retained deposits of active ingredients on leaf surfaces are directly related to emulsion stability, amount of emulsifier and droplet size of spray emulsion. From the data obtained, it was found that the stability of emulsion must be balanced with other physical properties. The emulsion should remain contact in the spray tank but should break almost instantly on contact with foliage, etc. upon being sprayed. When this happens the toxic agent forms a film on the surface and is not easily removed. If the emulsion does not break, much of the material drift off and serves no useful purpose. By the same token, the droplet size of spray emulsion is important. If the spray emulsion droplets are too fine, breaking on contact with foliage tends to be incomplete, while if the droplets are large, creaming will take place, causing uneven distribution of the material on the target area [60].

The cationic surfactant (polyoxyethylene (5) alkyl amino) and nonionic surfactant (polyoxyethylene (8-9) nonylphonol) increased the activity of glyphosate and increased the deposition on the difficult to wet wheat plants by 2-3 fold, whereas the surface tension is unaltered [61].

Surfactants facilitated wetting, spreading, dispersing, solubilizing and emulsifying, besides other surface modifying properties to bring about enhanced herbicidal action. Also, surfactants are commonly used in formulation of foliar applied agrochemicals to improve physical / chemical properties of the spray solution and to enhance uptake [62, 63].

The activator surfactant could alter the permeability of plant cuticle, thus improve the effectiveness of pesticide which has to penetrate it, in order to be biological active [64].

The influence of surfactants as Triton x-114, a nonionic surfactant prepared on foliar retention of pesticide used in forestry: premthrin, fenitrothion, *bacillus thuringinesis*, (B,T) and diflubenzuron was studied. Result obtained indicated that emulsion stability of permethrin and fenitrothion increased with increasing surfactant level while the emulsion drop size decreased with all tank mixes, a direct relationship was observed between the mass of liquids retained on the foliage and liquid viscosity. In contrast, the amount of pesticide retained was unaffected by viscosity but was influenced by emulsion droplet size initially, the amount of pesticide retained on the foliage increased with increasing surfactant concentration, beyond optimum surfactant level, the emulsion drop sizes were to small and the emulsions become too stable to allow maximum [65].

The effect of surfactant on pesticide penetration at the cuticle of the plant according to separation, deposition, portion coefficient and other factors. They managed to determine the amount of pesticide penetrated inside the cuticle by the effect of surfactant, so by known the rate of penetration and permeability of cuticles, the determined a limit does can be used [66].

The effect of mono- disperse ethoxylated alcohol on the mobility of 2.4 dichlorophenoxy acetic acid (2.4-D) in cuticular membrances from bitter orange, pear, green pepper and tomatoes, indicated that the surfactant increase the mobility by time and was inversely proportional to the (2.4 – D) in cuticles prior to surfactant treatment. As the molecular weight of surfactants increased their effects decreased and the time dependence of effect becomes more pronounced. Susceptibility of cuticle to surfactant treatment varied among plant species [67].

The effect of surfactant, PEG 600 DL, on the physical and biological efficacy of two pesticides i.e. profenofos 72% EC, and fenpropathrin 20% EC against the 4^{th} instar larvae of *S. littoralis* was studied. The obtained data indicated that the surfactant gave a slight change in the physical properties of pesticide by decreasing pH value and increasing viscosity of spray solution so the deposit and efficiency of each pesticide increased [68].

The tested surfactants, AYM and AYD, increased the toxicity and insecticidal activity of spray solution of insecticides (Curacron, Sumialpha and Deenate). This pesticidal effect could be attributed to the increase in toxicity and deposits of tested insecticides on the treated plant leaves as a result of the action of surfactant to improve their physico- chemical properties, such as increase of both viscosity and electric conductivity and decrease of both pH value and conductivity [69].

Surfactants increased penetration of herbicide, which causes more activity because of interaction with herbicide and changing the surface chemical properties of spray solution as well as changing the physical nature of plant itself. The use of surfactants in the spray solution helps the spray to adhere to the plant. Most plants have wax, like coating on the exterior that causes water to bead up. A surfactant is detergent like substance that is added to a spray mixture to cause the liquid to disperse a cross the plant surface better electrostatic sprayers create a positive electrical charge that is attracted by a negative charge on the plant. These causes the spray droplets to go directly to the plant surface and stick resulting in a lower volume of pesticides and less contact with the ground droplet adhesion, spreading and retention on leaf and seed surfaces are studies in the presence of surfactants for successful formulation of herbicide whereby efficient coverage less wastage and environment protection are achieved [70, 71].

1-6-2- Viscosity of spray solution

When the viscosity of spray solution increased as a result of using thickening or sticking agents or as a result of any adjuvant used in preparation of the pesticides as suitable formulation, the following effects are occurred as a result of increasing the viscosity of spray solution:

Several new adjuvants as drift control agents as polysaccharide – gum, having pseudoplastic and thixotropic properties, an alignate derivative (keltex) and dry granular swellable polymer (norback) producing a particulate solutions, and hydroxyl ethyl cellulose (vistik) with visco-elastic properties, in order to modify the viscosity of agricultural spray [72].

The effect of foliar sticker on increasing the residual activity of carbaryl. Their results indicated that the intial deposit one hour after application was 370.01 ppm. This value dropped to 264.33 ppm one day after treatment. Residues, then decreased gradually, and 246.13, 182.60, 117.86, 101.60 and 67.34 ppm were detected after 1, 4, 8, 12, and 15 days from treatment, respectively. They concluded that sticker UCL in the spray solution at the rate of 500 ml/ feddan protected carbaryl residue from rapid decrement [73].

3 – 4% of sprayed materials drifted away from the target area as droplets, and that 25.30 % of the sprayed butyl ester of 2,4 – D was lost as vapour within half an hour of spraying. The proportion of herbicide drifting as droplets could be reduced by designing equipment producing a low proportion of small droplets or by changing the viscosity of spray solution by using additives [74].

Effectiveness of two thickening agents, norback and vistik, evaluated in controlling spray drift. He found that the proportion of herbicide drifting as droplets can be reduced by changing the viscosity of spray solution by using thickening agents. Norback reduced drift by 63%, while vistik gave up to 98% control. Time after addition of thickening agent to solution and temperature had little effect on viscosity of the mixture [75].

Polyvinyl thickening material Naclo-trol was used for controlling spray drift. Naclo-trol increased the viscosity of spray liquid. It markedly changed the droplet-forming process, producing a droplet spectrum with few small drops. Naclo-trol was less salt sensitive than most of the other thickeners, but it also reduced the rate of evaporation of the droplet by about 30 %. The total spray loss was reduced when the thickener was used, the total spray loss ranged from 2.9 to 23.9% with thickener. In general, low concentrations of thickener decreased total drift deposit by 15 to 50 % and high concentrations of thickener decreased total drift deposit by 70 to 80%. The increase of viscosity of spray solution would increase the deposit on the treated plant leaves, reduce the drift and increase the efficiency [76].

The polyvinyl polymer spray additive increased the size and stability of spray droplets solution in field trials. The polymer decreased the drift of agriculture sprays applied by ground equipment for 90% without affecting the nozzle output or markedly affecting the droplet spectrum. Selectivity and performance trials showed that the polymer had only minor effects on herbicide activity. Favorable physical properties ease of mixing and low rate required of the herbicide (30 – 60 ml/100 liters) were among the advantages claimed. The polymer appeared to act by increasing the shear strength of the spray solution, thus a reduction in the proportion of the spray stream which was sheltered by edges of nozzle and therefore liable to drift [77].

Sticker adjuvants, including exhalt, NU-film 17, plant- card, plyace, stretcher and triton x-100, used for increasing viscosity and the persistence of chlorpyrifos, chlorpyrifos- methyl and Lindane on the solution pine beetle were effective in improving the persistence and Lindane up to 4 months post-treatment [78].

The addition of 0.004 kg of permethrin or fenvalerate per ha to the polybutene sticker, Bio-Toc, increased the viscosity of solution then increased the effectiveness of the treatment [79].

Additives such as triethylene glycol dimethyl ether, diethylene glycol dibutyl ether (DEG-AB), diethyl butyl malonate (DE-BM) and tetraethylene glycol dimethyl ether (tet EG-DM) increased the evaporation rate and increased the residual effect of trimedlure isomer (TML-c) against *Ceratitis capitata* [80].

1-6-3- Elecrical conductivity of spray solution

The increase of electrical conductivity of pesticidal spray solution would lead to deionization in the treated plant surface, and then increase the pesticidal efficiency [81].

The most physical compatible additives such as emulsifier/3 increased the toxicity and insecticidal activity of candidate insecticide spray solutions (deenate, carbaryl, thiodicarb and cyanophos) this synergistic effect could be attributed to the increase in toxicity and deposits of tested insecticides on the treated plant leaves as a result of the action of additives to improve their physico-chemical properties, such as increase of electric conductivity of the spray solution [82].

1-6-4- pH value of spray solution

The high alkalinity of spray solution can lead to hydrolysis of pesticide active ingredient causing reduce in their effectiveness [83].

Alkaline hydrolysis is an irreversible chemical reaction in which OH— (hydroxyl ions) break pesticide chemical molecules apart, reducing them to other chemicals having no pesticidal qualities. Hydrolysis occurs whenever sensitive pesticides such as organophosphates, carbamates, and synthetic pyrethroids are put into alkaline spray solutions. A safe spray solution pH for most pesticide chemicals is probably between 4.5 and 7.5 with the best probably between 5.0 and 6.0 [84].

The addition of two foliar fertilizers, Complesal and Wuxal, to two spray oils, Masrona 4 and Super royal c, decreased the pH value of the spray solution from 7.5 to 7.3 and 7.2, respectively, for Masrona 4 and 7.7 to 7.5 and 7.2, respectively for super royal c . The retention of Masrona 4 and Super royal C with Complesal and Wuxal increased from 1.143 and 1.1 mg/cm^2, respectively, to 1.409, 1.66 for Masrona 4 and 1.448 and 1.587 mg/cm^2, respectively, for Super royal C. This decrease in pH value and increase in the retention will lead to increasing the insecticidal efficiency of spray oils. The decrease in pH value of insecticide spray solution indicates an increase in positive charge of spray solution leading to increasing attraction between spray solution and the treated plant leaves surface, which have negative charges, then will increase the retention and the insecticidal efficiency [85].

1-7- Specifications of the residue limits of the different pesticides

i- Chlorpyrifos

Codex 2008, found that the maximum residue limits (MRL) of chlorpyrifos on cotton plant is 0.05 ppm, where preharvest intervals (PHI) is 14 days according to the Egyptian Agriculture Pesticides Committee recommendations, since residue of chlorpyrifos in cotton plant after this period become equal or less than the recommended MRL, where acceptable daily intake (ADI) was found to be 0.01 mg/Kg b.w. [28].

ii- Methomyl

Codex 2008, found that the maximum residue limits (MRL) of methomyl on cotton plant is 0.1 ppm, where preharvest intervals (PHI) is 7 days according to the Egyptian Agriculture Pesticides Committee recommendations, since residue of methomyl in cotton plant after this period become equal or less than the recommended MRL, where acceptable daily intake (ADI) was found to be 0.02 mg/Kg b.w. [28].

iii- Copper oxychloride

Codex 2008, found that MRL of copper oxychloride on onion plant is 20 ppm, where PHI is 20 days according to the Egyptian Agriculture Pesticides Committee recommendations, since residue of copper oxychloride in cotton plant after this period become equal or less than the recommended MRL, where ADI was found to be 0.015 mg/Kg b.w. [28].

vi- Glyphosate isopropyl ammonium

Codex 2008, found that the MRL of glyphosate is 0.2 ppm, where PHI is 14 days according to the Egyptian Agriculture Pesticides Committee recommendations, since residue of glyphosate in cotton plant after this period become equal or less than the recommended MRL, where ADI was found to be 0.3 mg/Kg b.w. [28].